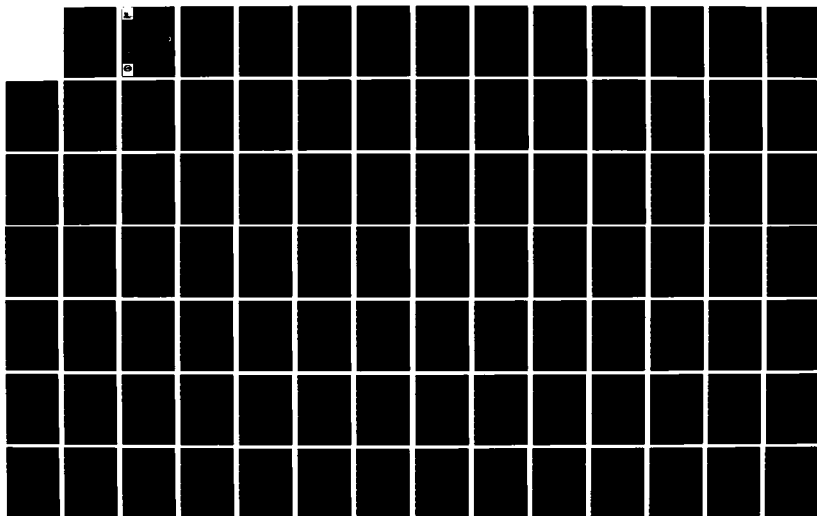
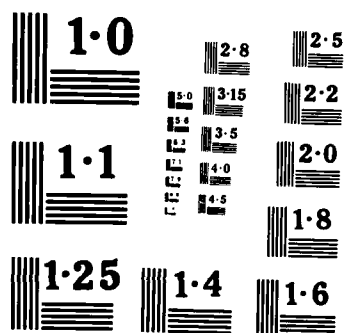


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US Army Corps
of Engineers

AD-A158 817

TECHNICAL REPORT EL-85-7

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GUIDELINES FOR WATER QUALITY LABORATORY OPERATIONS

by

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20. ABSTRACT (Continued).

operations. This report contains information which will be helpful to both personnel working in water quality laboratories and to personnel responsible for monitoring water quality laboratory contracts.

Many information sources are given to include contacts with the US Environmental Protection Agency, US Geological Survey, and the CE. Many basic references are also given which cover all aspects of water quality laboratory operations.

Techniques in sample collection and sample handling are given along with recommended and approved methods for sample analysis. There is a section addressing laboratory quality assurance and quality control which can be used from both an operational and monitoring standpoint.

A survey of CE water quality laboratory capabilities was taken and the results are presented. From the survey the most often performed analyses in CE laboratories were obtained. A discussion of these analyses and potential problems with these analyses is presented.

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PREFACE

This report was prepared at the US Army Engineer Waterways Experiment Station (WES), Vicksburg, Miss., from October 1983 to September 1984. Study information was received from personnel of the Environmental Laboratory (EL) Analytical Laboratory Group (ALG): Mmes. A. B. Strong, L. K. Stevenson, A. F. Duke, J. M. Christian, E. M. McLemore, K. F. Myers; and Messrs. R. A. Karn, D. R. Brown, G. M. Warren, W. L. Tyler, Jr., and B. N. Brown. Messrs. M. John Cullinane, Jr., and Jerry N. Jones, of the Water Supply and Waste Treatment Group (WS&WTG), performed the literature review and wrote the report.

The study was under the general supervision of Mr. N. R. Francingues, Jr., Chief, WS&WTG; Mr. A. J. Green, Jr., Chief, Environmental Engineering Division; and Dr. J. Harrison, Chief, EL.

Funding for the study was provided by the Office, Chief of Engineers (OCE), and the OCE Technical Monitor was Mr. B. V. Moran.

During the preparation of this report, COL Tilford C. Creel, CE, and COL Robert C. Lee, CE, were Commanders and Directors of WES and Mr. F. R. Brown was Technical Director. At the time of publication, COL Allen F. Grum, CE, was Director and Dr. Robert W. Whalin was Technical Director.

This report should be cited as follows:

Jones, J. N., and Cullinane, M. J., Jr. 1985. "Guidelines for Water Quality Laboratory Operations," Technical Report EL-85-7, US Army Engineer Waterways Experiment Station, Vicksburg, Miss.

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CONVERSION FACTORS, NON-SI TO SI (METRIC)
UNITS OF MEASUREMENT

Non-SI units of measurement used in this report can be converted to SI
(metric) units as follows:

<u>Multiply</u>	<u>By</u>	<u>To Obtain</u>
cubic feet	0.02831685	cubic metres
feet	0.3048	metres
inches	25.4	millimetres
linear feet	0.3048	metres
square feet	0.09290304	square metres

GUIDELINES FOR WATER QUALITY LABORATORY OPERATIONS

PART I: INTRODUCTION

Background

1. Corps of Engineers (CE) requirements for the analysis of water quality samples are satisfied through the use of a combination of in-house and contract services. The CE currently has thirteen water quality laboratories consisting of three District laboratories, seven Division laboratories, and three research and development (R&D) laboratories. Analytical needs beyond the capability of a specific laboratory are satisfied through special contracted services from other CE laboratories, other governmental agencies, or commercial laboratories.

2. Due to funding and personnel restrictions, CE laboratories are reporting a decline in their water quality analysis requirements. For most CE laboratories, remaining at the status quo, in terms of staff and workload, would be considered a very positive yet unrealistic outlook.

3. When consideration is given to the total CE project funding level, \$3.5 to \$4 million for water quality analysis may seem rather minor. However, when one considers the possible effects of inaccurate and imprecise data upon the various CE projects, the significance of the water quality analyses is increased many times above the initial cost. It is necessary, therefore, to make every possible effort to ensure good communication among the various CE laboratories concerning analytical methodology problem areas and quality assurance and quality control (QA/QC) procedures.

Objectives

4. The primary objectives of this paper are to:
 - a. Present information concerning analytical methodologies and QA/QC procedures which may be helpful to the operation of CE water quality laboratories.
 - b. Provide information on possible trouble spots to look for in the analytical procedures most used by CE water quality laboratories.

- c. Provide information on CE water quality laboratory capabilities.
- d. Provide sources for detailed information concerning sampling, sample handling procedures, QA/QC procedures, and analytical methodologies.

5. A secondary objective is to improve communications among the CE water quality laboratories. Hopefully, this report will spawn more communication between the laboratories so that the CE as a whole can be served more effectively in the area of water quality analysis.

Approach

6. Each CE District, Division, and R&D laboratory completed a survey which outlined their major work areas and capabilities. This information was compiled into tables for presentation. No conclusions concerning the quality of a laboratory were intended, nor could any viable conclusions concerning quality be drawn from the information presented.

7. A literature search was performed that accentuated two basic topics: (a) sources of water quality analysis information, and (b) water quality sample handling and analysis techniques. These topics were emphasized in order to produce helpful guidance for problems which may be encountered in CE water quality laboratories. Everything in this report will not be new or relevant to every CE laboratory. However, if the CE water quality laboratories benefit from even one portion of the report, the objectives will have been met and the communication effort considered a success.

Organization of Report

8. This report is divided into five basic divisions which occur in much the same order as the life of a water quality sample. Before a sample is taken a water quality laboratory must plan for it and assess the laboratory's capabilities. This step corresponds with the CE laboratory capabilities and information sources portions of this report (Parts II and III). Sample collection, preservation, and shipping are all very important in the life of a sample and are stressed as the second major division of this report (Part IV). Sample preparation and analysis is the next step and the third major division of this report (Part V). Quality control and quality assurance are factors

which must permeate the entire life of a sample. They are presented as the fourth major division (Part VI) but should be foremost in the minds of every sampler, analyst, and laboratory director, and should begin in the very early planning stages. Part VII (the fifth major division) emphasizes potential problem areas and interferences with the analytical process. The report concludes with a summary and recommendations (Part VIII) and six appendices which present many informational sources, publications, and approved analytical methodologies.

PART II: CORPS OF ENGINEERS WATER QUALITY LABORATORY CAPABILITIES

Background

9. CE water quality laboratories perform a wide range of environmental chemical analyses. Many variables, both objective and subjective, must be considered when assessing the capabilities of a water quality laboratory. In this chapter an objective presentation is made of the CE water quality laboratories' capabilities in terms of typical analyses routinely performed, instrumentation and equipment, personnel, and physical size. There is no intention nor attempt made to rank the laboratories in terms of capabilities but simply to present some of the physical capabilities of each laboratory. In most cases when a particular analysis is not shown for a certain laboratory the correct assumption would be that the laboratory does not perform that analysis on a routine basis and not that the laboratory does not possess the capability to perform the analysis. This is especially true for the simpler physical analyses which are not shown for some laboratories (e.g. solids, temperature, color, etc.).

Typical Analyses

10. The CE water quality laboratories have the combined capability for almost any standard environmental chemical analysis procedure. Tables 1-4 are inventories of the various analyses which are routinely performed by the three District laboratories, seven Division laboratories, and three R&D laboratories. Table 1 presents typical analytical tests for physical and microbiological characteristics of environmental samples. Table 2 presents typical analytical tests for nonmetallic ions and nutrients. Table 3 presents tests for metallic ions. Table 4 presents tests for typical organic parameters. The numbers in parentheses in Tables 1-4 indicate the total number of laboratories, out of the thirteen CE water quality laboratories, which routinely perform the indicated analysis.

Table I

Typical Analytical Tests for Physical and Microbiological Characteristics

Parameter	District Laboratories			Division Laboratories							R&D Laboratories		
	Kansas City	New Orleans	St. Louis	Missouri River	New England	North Pacific	Ohio River	South Atlantic	South Pacific	Southwest	CERL	CRREL	WES
Color (7)	-	-	-	X	X	X	-	X	X	X	X	-	-
Conductivity (8)	-	-	-	X	X	X	-	X	X	X	X	X	-
Dissolved oxygen (5)	-	-	-	-	X	X	-	-	-	-	X	X	X
pH (10)	X	-	-	X	X	X	-	X	X	X	X	X	X
Total dissolved solids (9)	-	-	-	X	X	X	X	X	X	-	X	X	X
Total solids (10)	-	-	-	X	X	X	X	X	X	X	X	X	X
Total suspended solids (9)	X	-	-	X	-	X	X	X	X	-	X	X	X
Volatile suspended solids (6)	-	-	-	-	-	-	X	-	X	X	X	X	X
Temperature (3)	-	-	-	-	X	-	-	X	-	-	X	-	-
Turbidity (9)	X	-	-	X	X	X	-	X	X	-	X	X	X
Particle size (4)	-	-	-	-	-	-	X	X	-	-	X	-	X
Redox potential (0)	-	-	-	-	-	-	-	-	-	-	-	-	-
Total coliform (3)	X	-	-	-	X	X	-	-	-	-	-	-	-
Fecal coliform (3)	X	-	-	-	X	X	-	-	-	-	-	-	-
Fecal strep (2)	X	-	-	-	X	-	-	-	-	-	-	-	-

* CERL = Construction Engineering Research Laboratory; CRREL = Cold Regions Research Engineering Laboratory; WES = US Army Engineer Waterways Experiment Station.

Table 2

Typical Analytical Tests for Nonmetallic Ions and Nutrients

Parameter	District Laboratories				Division Laboratories					RD Laboratories		
	Kansas City	New Orleans	St. Louis	Missouri River	New England	North Pacific	Ohio River	South Atlantic	South Pacific	Southwest	CERL	CRREL WES
Acidity (6)	-	-	-	X	X	X	X	-	X	-	X	-
Alkalinity (11)	X	-	-	X	X	X	X	X	X	X	X	X
CO ₂ (Free) (1)	-	-	-	X	-	-	-	-	-	-	-	-
Chloride (12)	X	X	-	X	X	X	X	X	X	X	X	X
Cyanide (6)	-	-	-	X	-	X	X	-	X	-	X	X
Fluoride (8)	-	-	-	X	X	X	X	X	X	-	X	X
Sulfide (6)	-	-	-	X	X	X	X	-	X	-	X	-
Sulfate (10)	-	-	-	X	X	X	X	-	X	-	X	-
Ammonia (10)	-	-	-	X	X	X	X	X	X	X	X	X
Nitrate (10)	-	-	-	X	X	X	X	X	X	X	X	X
Nitrite (9)	-	-	-	X	X	X	X	X	X	-	X	X
Total Kjeldahl Nitrogen (13) (10)	-	-	-	X	X	X	X	X	X	X	X	X
Total phosphate (10)	-	-	-	X	X	X	X	X	X	X	X	X
Orthophosphate (9)	-	-	-	X	X	X	X	X	X	X	X	X
Silicates (6)	-	-	-	X	-	X	X	X	X	-	X	-

Table 3
Typical Analytical Tests for Metallic Ions

Parameter	District Laboratories			Division Laboratories				R&D Laboratories		
	Kansas City	New Orleans	St. Louis	Missouri River	New England	North Pacific	Ohio River	South Atlantic	South Pacific	South west
Aluminum (8)	-	-	-	x	x	x	x	x	x	x
Antimony (3)	-	-	-	x	-	-	x	-	x	-
Arsenic (8)	-	-	-	x	x	x	x	x	x	x
Barium (7)	-	-	-	x	x	x	x	-	x	x
Beryllium (7)	-	-	-	x	x	x	x	-	x	x
Bismuth (3)	-	-	-	-	x	-	x	-	x	-
Boron (5)	-	-	-	x	x	-	x	-	x	-
Calcium (10)	-	-	-	x	x	x	x	x	x	x
Cadmium (10)	-	-	-	x	x	x	x	x	x	x
Chromium (10)	-	-	-	x	x	x	x	x	x	x
Cobalt (8)	-	-	-	x	x	-	x	x	x	x
Copper (10)	-	-	-	x	x	x	x	x	x	x
Hardness (11)	x	-	-	x	x	x	x	x	x	x
Iron (10)	-	-	-	x	x	x	x	x	x	x
Lead (10)	-	-	-	x	x	x	x	x	x	x
Lithium (3)	-	-	-	x	-	-	x	-	x	-
Magnesium (9)	-	-	-	x	x	x	x	x	x	x
Manganese (10)	-	-	-	x	x	x	x	x	x	x
Mercury (9)	-	-	-	x	x	x	x	x	x	x
Molybdenum (4)	-	-	-	x	x	-	x	-	x	-
Nickel (10)	-	-	-	x	x	x	x	x	x	x
Potassium (10)	-	-	-	x	x	x	x	x	x	x
Selenium (9)	-	-	-	x	x	x	x	x	x	x
Silicon (3)	-	-	-	-	x	-	x	-	x	-
Silver (9)	-	-	-	x	x	x	x	x	x	x
Sodium (9)	-	-	-	x	x	x	x	x	x	x
Strontium (3)	-	-	-	-	x	-	x	-	x	-
Tin (5)	-	-	-	x	-	-	x	-	x	-
Titanium (4)	-	-	-	x	x	-	x	-	x	-
Uranium (2)	-	-	-	x	-	-	x	-	x	-
Vanadium (4)	-	-	-	x	x	-	x	-	x	-
Zinc (10)	-	-	-	x	x	x	x	x	x	x

Table 4
Typical Analytical Tests for Organics*

Parameter	District Laboratories				Division Laboratories				R&D Laboratories			
	Kansas City	New Orleans	St. Louis	Missouri River	New England	North Pacific	Ohio River	South Atlantic	South Pacific	Southwest	CERL	WES
Biochemical oxygen demand (BOD) (5)	-	-	-	x	-	-	-	-	x	-	x	x
Chemical oxygen demand (COD) (10)	-	-	-	x	x	x	x	x	x	x	x	x
Chlorophyll-a (4)	-	-	-	x	x	-	-	-	-	-	x	-
Oil and grease (10)	-	-	-	x	x	x	x	x	x	x	x	x
Phenol (8)	-	-	-	x	x	x	x	-	x	x	x	x
Total organic carbon (TOC) (10)	x	-	-	x	x	-	x	x	x	x	x	x
Polychlorinated biphenyls (PCB) (9)	-	-	-	x	x	-	x	x	x	x	x	x
Pesticides (GC) (8)	-	-	-	x	x	-	x	x	-	x	x	x
Pesticides (GC/MS) (6)	-	-	-	x	-	-	x	x	x	-	-	x
Herbicides (GC) (8)	-	-	-	x	-	-	x	x	x	x	x	x
Volatile organics (GC/MS) (5)	-	-	-	x	-	-	x	-	x	-	-	x
Base neutral extractables (GC/MS) (4)	-	-	-	x	-	-	x	-	x	-	-	x
Acid extractables (GC/MS) (4)	-	-	-	x	-	-	x	-	x	-	-	x

* GC = gas chromatography; MS = mass spectrometry.

Laboratory Attributes

Instrumentation and equipment

11. Modern water quality laboratories rely heavily upon automated and semiautomated analytical instrumentation. Tables 5 and 6 show the types of instrumentation and general equipment found in the CE water quality laboratories. In Table 5, instrumentation is defined as a device designed to provide specific analytical data. In Table 6, laboratory equipment is defined as support devices designed to aid in the process of obtaining analytical data but which do not directly provide the data.

Personnel

12. When one considers the magnitude of the chemical analysis effort within the CE, the number of personnel directly concerned with chemical water quality analysis is very limited. There are numerous reasons for the paucity of water quality laboratory personnel but personnel cutbacks and hiring restrictions are at the top of the list. Table 7 is a summary of personnel in CE water quality laboratories. CE water quality laboratories employ an average of four personnel including three to four chemists and one technician. The chief chemist generally acts as laboratory supervisor. The average experience level of the CE water quality chemist is 10.82 years. Table 7 is subject to change as personnel changes occur.

13. Appendix A is a listing of points of contact for CE water quality laboratories.

Physical size

14. Space requirements vary with the type of work being performed. Laboratory space requirements in research laboratories should be generally 215 to 275 sq ft* per worker, while for routine analytical laboratories 160 to 215 sq ft per worker is sufficient (Grover and Wallace 1979). Table 8 shows the available space for CE laboratories. When comparing number of personnel with available laboratory space, the CE laboratories far exceed the requirements previously stated. This situation occurs most likely because of too few personnel rather than too much laboratory space.

* A table of factors for converting non-SI units of measurement to SI (metric) is presented on page 5.

Table 5

Water Quality Laboratory Instrumentation

Instrument	District Laboratories				Division Laboratories							R&D Laboratories	
	Kansas City	New Orleans	St. Louis	Missouri River	New England	North Pacific	Ohio River	South Atlantic	South Pacific	Southwest	CERL	CRREL	WES
pH meter	4	3	3	1	10	1	1	2	2	1	3	6	3
Ion specific electrode(s)	-	3	-	4	3	1	1	1	1	1	4	3	6
Redox electrode	-	3	-	1	-	-	-	1	-	-	1	6	4
Balances	2	4	1	3	4	8	2	2	4	5	2	10	4
Conductivity meter	4	-	2	1	5	2	1	1	1	1	1	2	3
Nephelometers	3	1	2	1	3	1	-	1	-	1	2	-	1
Colorimeter	-	1	-	1	1	1	1	2	-	-	2	-	1
Spectrophotometer (ultraviolet-visible)	-	1	1	1	2	3	6	2	4	1	2	4	1
Spectrophotometer (flame emission)	-	1	1	1	1	2	1	1	-	-	1	3	-
Atomic absorption	-	2	1	2	1	2	2	1	2	2	1	2	4
Graphite furnace	-	2	1	1	1	-	1	1	1	1	1	2	2
Mercury cold vapor	-	-	-	1	1	-	1	1	1	-	-	1	1
Hydride system	-	-	-	1	1	-	1	1	-	1	-	1	1
Auto analyzer	-	2	1	1	1	-	3	1	1	-	11	6	4
Carbon analyzer	-	1	-	1	1	1	1	1	1	1	2	1	1
ICAP or DC plasma arc emission spectrophotometer*	-	-	-	1	-	-	1	-	1	-	-	-	1
Infra-red analyzer	-	-	-	1	1	1	1	1	1	-	1	1	-
Gas chromatograph	-	2	-	3	2	1	1	1	2	1	3	5	4
Liquid chromatograph	-	1	-	-	-	-	-	-	-	-	1	2	1
Anodic stripping unit	-	-	-	-	-	-	-	1	-	-	1	1	-
Polarographic analyzer	-	-	-	-	-	-	-	-	-	-	1	1	-
Mass spectrophotometer	-	1	-	1	-	-	1	-	1	-	-	1	2
Titrimeters-coulometric	-	3	-	1	-	-	-	-	-	-	1	1	1
Computerized analyzer	-	-	-	-	-	-	1	-	-	-	-	-	-
Total organic halides	-	-	-	-	-	-	-	-	-	-	1	-	-
Ion chromatograph	-	-	-	-	-	-	-	-	-	-	-	1	-

* ICAP = Inductively coupled argon plasma. DC = Direct current.

Table 6
Water Quality Laboratory Equipment

Equipment	District Laboratories			Division Laboratories					R&D Laboratories			
	Kansas City	New Orleans	St. Louis	Missouri River	New England	North Pacific	Ohio River	South Atlantic	South Pacific	Southwest	CERL	CRREL WES
Ovens:												
25° - 200°C	1	3	2	-	3	6	4	4	4	1	1	-
200° - 300°C	-	-	-	3	-	1	-	-	1	1	1	3
300° - 400°C	-	-	-	-	-	-	-	-	-	-	1	-
400°C	-	-	-	-	-	2	-	-	-	-	1	1
Furnaces	-	2	1	1	1	3	1	3	2	2	3	2
Sample storage												
Walk in refrigerator, sq ft	-	120	-	36	64	Use cold	-	108	414	-	-	1-UNK 56
Refrigerator, cu ft	-	50	43	14	47	Cabinets	3	-	71	90	12	20
Freezer, cu ft	-	26	-	-	56	-	-	-	115	-	-	15
Environment controlled room	-	-	-	300	-	-	-	-	324	-	2-80	-
sq ft												
Fume hoods (number and length)												
Transite	-	-	4', 6'	2-20'	8'	10', 15'	4-6'	2-7', 4', 8'	2-6'	-	3-5'	5-6', 4-4'
Fiberglass	6'	4-59"	-	-	-	-	-	-	-	-	-	-
Stainless steel	-	-	-	-	-	3-5'	-	-	1-12'	-	-	-
Perchloric acid	-	1-59"	-	-	-	-	-	-	-	-	-	6'
Distillation unit	1	1	-	1	1	1	-	-	1	1	1	1
Deionization unit	-	1	1	2	-	1	1	1	1	1	1	1
Centrifuge	-	2	1	2	3	3	1	2	3	3	1	2
Vacuum filter system	2	aspir.	2 pumps	pump	-	-	pump	aspir.	aspir.	-	1	1

Table 7
Personnel Summary for CE Water Quality Laboratories

<u>Laboratory</u>	<u>Personnel Classification</u>			<u>Total</u>
	<u>Chemist</u>	<u>Technician</u>	<u>Other</u>	
District Laboratories				
New Orleans	2	2	-	4
St. Louis	1	-	-	1
Kansas City	1	2	2*	5
Division Laboratories				
Missouri River	3	-	-	3
New England	3	1	1*	5
North Pacific	1	1	-	2
Ohio River	3	1	2**	6
South Atlantic	1	2	-	3
Southwest	2	-	-	2
South Pacific	2	1	-	3
Research Laboratories				
CERL	3	-	-	3
CRREL	4	3	-	7
WES	5	4	1†	10

-
- * Biologists.
 ** Co-op students.
 † Mathematician.

Table 8
Water Quality Laboratory Space Availability

<u>Laboratory</u>	<u>Office sq ft</u>	<u>Laboratory sq ft</u>	<u>Laboratory Space per Person sq ft</u>	<u>Bench lin ft</u>	<u>Other sq ft</u>
Kansas City	*	1540	308	88	-
New Orleans	360	2800	700	368	460
St. Louis	476	2000	2000	140	-
Missouri River	364	5000	1667	270	-
New England	588	2550	510	225	-
North Pacific	40	800	400	88	-
Ohio River	150	1876	313	128	-
South Atlantic	121	1739	580	125	-
South Pacific	450	2840	947	206	-
Southwest	175	2100	1050	180	-
CERL	155	925**	308	240**	-
CRREL	NR†	NR	NR	NR	NR
WES	1825	4000	400	450	-

* Included in 1540 sq ft of lab space.

** Includes 25 sq ft of space and 25 lin ft of bench space in mobile lab.

† NR = Not reported.

PART III: INFORMATION SOURCES FOR LABORATORY OPERATIONS

Background

15. Each CE laboratory has particular sources which are used to obtain information on such topics as sample collection, sample shipping, sample preparation, sample analysis, instrumentation, and QA/QC procedures. These sources vary from personal contacts and publications to different governmental agencies and private institutions. All of these topics and sources will be discussed in this chapter and hopefully some new information will be provided concerning sources where detailed information can be obtained on the various daily water quality laboratory needs and problems.

Personal Contacts

16. Undoubtedly each laboratory manager, chemist, and technician has personal contacts with which they are most comfortable and in which they place the most confidence. This is good but a word of caution must be offered concerning single sources of information. No one person knows everything about every aspect of a water quality laboratory's operations. Therefore, multiple sources of information should be solicited before a decision is made concerning certain aspects of the laboratory operations.

Government Agencies

Corps of Engineers

17. Some of the best sources of information are found in Appendix A which is the CE Water Quality Laboratories Points of Contact. Contrary to popular opinion, most problems encountered in the CE District and Division laboratories have at one time or another confronted one or all of the other CE District and Division laboratories. It therefore remains an enigma as to why there is not more consistent communication between laboratories within the CE. If the points of contact found in Appendix A are not completely familiar with a particular problem, in most cases one can be put in contact with someone else in the CE who is familiar with or has experienced the problem in question.

US Environmental
Protection Agency (USEPA)

18. The USEPA has the national policy-setting responsibility concerning matters related to water quality analyses and criteria. It is therefore logical that the USEPA would not only be a good source but a necessary source of information for all CE water quality laboratories. Appendix B is a listing of all the USEPA Regional QA Coordinators along with a map illustrating the ten Federal USEPA Regions.

19. USEPA Regional QA Coordinators for water and air are responsible for QA/QC activities in their respective region. They maintain liaison with the USEPA Environmental Monitoring and Support Laboratory (EMSL) in Cincinnati, Ohio; perform advisory and working group activities for methods selection; and are key persons for disseminating information on such matters as new or revised analytical methods, publications, and QC samples. Regional QA Coordinators can provide information about the USEPA Quality Control Sample Program and the USEPA Repository for Toxic and Hazardous Materials.

20. Appendix C is a listing of all EPA Technical Information Program Managers and the Technical Information Managers at the various USEPA Environmental Research Laboratories throughout the country. These people are at least good starting points for obtaining technical information concerning water quality laboratory operations.

US Geological Survey (USGS)

21. Another government agency which is a good source of water quality information is the USGS. The best information sources within USGS include:

US Geological Laboratory
Denver Central Laboratory
5293 Ward Road
Ervada, CO 80002
FTS: 234-4992
COML: 303-234-4992

US Geological Survey
National Water Quality Laboratory
6481 Peach Tree Industrial Blvd.
Suite H
Doraville, GA 30340
FTS: 242-4806
COML: 404-221-4806

US Geological Survey Library - Distribution
950 National Center
Reston, VA 22092
FTS: 928-6673
COML: 703-860-6673

US Geological Survey
Quality of Water Branch
412 National Center
Reston, VA 22092
FTS: 928-6834
COML: 703-860-6834

22. Appendix D presents additional USGS information sources. These sources range from the USGS Headquarters in Reston, Va., to the various regional hydrologist and research hydrologist offices throughout the United States. The most important USGS informational sources to CE water quality laboratories will most likely be the previously mentioned USGS National Water Quality Laboratories in Denver and Atlanta.

23. These agencies are not the only ones with available information but they are normally considered the major sources of water quality information within the government.

24. Each CE District and Division water quality laboratory should strive to improve communications with information sources within the District and Division jurisdictional boundaries. These information sources might include:

- a. Federal government agencies.
- b. State government agencies.
- c. Colleges and universities.
- d. Research institutes.
- e. Private contract laboratories.

Publications

Basic references

25. There are numerous publications available which address the many phases of the life of a sample before the actual evaluation of sample data (e.g. collection, shipping, preparation, analysis, and associated QA/QC procedures). Since each CE water quality laboratory has different personnel, it will develop its own characteristic personality, idiosyncrasies, and mode of

operation. In order for CE laboratories to maintain as much consistency as possible, certain "standard" publications should be used and incorporated into standard operating procedures. The "Basic References" section of Appendix E addresses all aspects of the water quality analysis cycle and should be available and in use in all CE water quality laboratories.

Specialty references

26. It is recognized that there is a vast quantity of literature concerning water quality analysis. To try to reference all the literature would be meaningless and unproductive. Granted, most water quality analysis problems can be solved using the methodologies referenced previously as standard procedures. However, there are situations that occur which require different or new methodologies to be used and/or developed. The "Specialty References" section of Appendix E includes those which, in addition to the ones previously mentioned, are used most often by the WES Analytical Laboratory Group (WES-ALG). These references have been found to be very useful depending upon the analytical problem encountered. The specialty references in Appendix E are listed by the subject matter which predominates the major portion of the reference. The specialty references are subdivided into: (a) analytical methodologies, (b) sample collection and handling, (c) laboratory quality assurance/quality control, (d) laboratory safety, and (e) training.

Pamphlets and periodicals

27. Standard journals as Analytical Chemistry, Journal of the Association of Official Analytical Chemists, Chemical Engineering News, etc., are well known and everyone has their own favorites. There are also a number of lesser known publications that are published on a monthly or quarterly basis which provide a lot of good, usable information to personnel associated with environmental chemical analysis. A listing of these publications containing more basic, day-to-day information is presented. Most of these publications are free of charge and are good sources of information on state-of-the-art instrumentation and laboratory operations.

Plasmaline
Beckman Instruments, Inc.
Spectroscopy Instruments Operations
Campus Drive at Jamboree Blvd.
P.O. Box C - 19600
Irvine, CA 92713
(714) 833-0751

News & Notes

Hach Co.
P.O. Box 389
Loveland, CO 80539

American Biotechnology Laboratory
International Scientific Communications, Inc.
808 Kings Highway
P.O. Box 827
Fairfield, CT 06430
(203) 576-0500

American Laboratory
808 Kings Highway
P.O. Box 827
Fairfield, CT 06430

Jarrell-Ash Plasma Newsletter
Allied Analytical Systems
One Burtt Rd.
Andover, MA 01810
(617) 470-1790
(800) 343-0322 - toll free

Computer Products
Gordon Publications
P.O. Box 14000
Dover, NJ 07801

Laboratory Equipment
P.O. Box 313
Dover, NJ 07801

The Bench Sheet (\$39/yr)
606 Quincy SE
Albuquerque, NM 87108
(505) 266-2778

Industrial Chemical News
633 Third Avenue
New York, NY 10164

Research and Development
Circulation Dept.
P.O. Box 5365
New York, NY 10150
(212) 605-9527

ORD Publications Announcement
ORD Publications
P.O. box 14249B
Cincinnati, OH 45214

Quality Assurance Newsletter
Betty J. Thomas
U.S. Environmental Protection Agency
Environmental Monitoring and Support
Laboratory - Cincinnati
Cincinnati, OH 45268
COML: (513) 684-7301; FTS: 684-7301

Supelco Reporter
Supelco, Inc.
Supelco Park
Bellefonte, PA 16823

Analytical Control
NUS Corporation
ATTN: Mrs. R. A. Cochran, Editor
Park West Office Center
Building II
Pittsburgh, PA 15275
(412) 788-1080

Industrial Hygiene News
Rimbach Publishing Inc.
8650 Babcock Blvd.
Pittsburgh, PA 15237

Pollution Equipment News
Rimbach Publishing Inc.
8650 Babcock Blvd.
Pittsburgh, PA 15237

Retention Times
Tracor Instruments
Tracor, Inc.
6500 Tracor Lane, Bldg. 27-4
Austin, TX 78721

Training Courses

28. Classroom and correspondence type training are available from several different sources. It should be noted that the information presented does not in any way constitute an endorsement of the organization offering the training, nor will any sort of judgment be presented regarding the merits of the training. The sponsoring organization should be contacted for further information. Some of the organizations offering training include:

Arizona State University
Chemistry Dept.
ATTN: Dr. Jacob Fuchs
Tempe, AZ 85287
(602) 965-4496
(602) 965-3461
Type: Classroom (modern industrial spectroscopy)

Savant
P.O. Box 3670
Fullerton, CA 92634
(714) 870-7880
Type: Correspondence (chemical analysis)

Heathkit Continuing Education
Heath Company
Benton Harbor, MI 49022
(616) 982-3411
Type: Correspondence (electronics,
BASIC programming)

The Center for Professional Advancement
P.O. Box H
East Brunswick, NJ 08816
(201) 249-1400
Type: Classroom (analytical chemistry,
analysis, engineering)

Perkin-Elmer Training Center
Main Ave.
Norwalk, CT 06856
(203) 762-1000
Type: Classroom and laboratory
(AA, ICAP, GC)

J. T. Baker Chemical Co.
ATTN: Carol Morris
Phillipsburg, NJ 08865
(201) 454-2500
Type: Classroom (safety, hazardous and
chemical waste disposal)

Finnigan MAT Institute
ATTN: Nancy Kranpitz
11 Triangle Park Drive
Cincinnati, OH 45246
(513) 772-5500
Type: Classroom (instrumental analysis)

American Chemical Society
Education Division
1155 16th St., N.W.
Washington, D.C. 20036
(202) 872-4588
Type: Classroom, correspondence (chemistry,
computers, statistics, analysis)

National Bureau of Standards
Training
Washington, DC 20234
(301) 921-3497, FTS: 921-3497
Type: Classroom (QA/QC, analysis)

American Society for Quality Control
230 W. Wells St.
Milwaukee, WI 53202
(414) 272-8575
Type: Classroom, correspondence (QA/QC)

29. It is not to be interpreted that the above organizations are the only sources, nor the best sources for training. Almost every major laboratory instrument producer has training available designed around their equipment. This is often outstanding training and should be taken advantage of to the fullest extent possible.

PART IV: SAMPLE COLLECTION, PREPARATION, AND SHIPPING

Background

30. It would be impossible to recommend specific "cookbook" procedures for every particular situation which may occur in CE water quality laboratories. Details concerned with locale, logistics, sample types, sample matrices, data use, and personnel often make it necessary for changes or modifications to be made in standard operating procedures. Even though changes may sometimes be necessary, there are still basic ideas and objectives which must be adhered to. This section will address those policies, in a general manner, which may be adapted to the many varying situations encountered by water quality personnel of the CE District and Division Offices.

Sample Collection

31. Sample collection is probably the least emphasized aspect of the water quality analysis scheme. This should not be the case, especially when one considers the importance and the objective of sampling. It must be remembered that the result of any analytical test procedure can be no better than the sample from which the result was obtained.

32. The objective of any sampling for chemical analysis is to collect a sample small enough to be easily handled yet large enough to be a true representation of the system from which it was taken and of sufficient quantity to provide the analyses needed. The implications are that the concentrations of components within the sample will be the same as in the system being sampled, and that the sample will not be significantly changed in composition before the analytical tests are performed.

33. A grab sample is defined as an individual discrete sample collected over a period of time not exceeding 15 min (Berg 1982). It can be taken manually using a pump, scoop, vacuum, or other suitable device. The collection of a grab sample is appropriate when it is desired to:

- a. Characterize water quality at a particular time.
- b. Provide information about minimum and maximum concentrations.
- c. Allow collection of variable sample volume.

- d. Corroborate composite samples.
- e. Meet a requirement of a discharge permit.

34. Grab samples are used when:

- a. The stream does not flow continuously such as batch dumps.
- b. The water or waste characteristics are relatively constant.
- c. The parameters to be analyzed are likely to change with storage.

35. A composite sample is defined as a sample formed by mixing discrete samples taken at periodic points in time or a continuous proportion of the flow. The number of discrete samples which make up the composite depends upon the variability of pollutant concentration and flow. A sequential composite is defined as a series of periodic grab samples each of which is held in an individual container, then composited to cover a longer time period. Six methods are used for compositing samples. Choice of composite type is dependent on the program and relative advantages and disadvantages of each composite type (Berg 1982). Samples should be composited when:

- a. Determining average concentrations.
- b. Calculating mass/unit time loading.

Surface water

36. If representative samples are to be taken and the sampling objectives met, then certain general guidelines must be followed. Some of the most important guidelines for obtaining representative surface water samples as reported by Berg (1982) are:

- a. Collect the sample where water is well mixed, that is near a Parshall flume or at a point of hydraulic turbulence such as downstream of a hydraulic jump. Certain types of weirs and flumes tend to enhance the settling of solids upstream and accumulate floating solids and oil downstream; therefore, such locations should be avoided as a sample source. For low level turbulence, mechanical or air mixing should be used to induce turbulence except when dissolved gases or volatile materials are being sampled.
- b. Collect the sample in the center of the channel at 0.4 to 0.6 ft depth from the bottom where the velocity of flow is average or higher than average and the chance of solids settling is minimum. This depth avoids bottom bed loads and top floating materials such as oils and grease.
- c. In a wide channel, divide the channel cross section into different vertical sections so that each section is equal in width. Take a representative sample in each vertical section.

- d. In a deep stream or lake, collect the samples at different depths. In those cases of wide and deep streams the samples can be composited or analyzed individually depending upon the program objective.
- e. When manual sampling with jars, place the mouth of the collecting container below the water surface and facing flow to avoid an excess of floating material. Keep the hand away from the mouth of the jar as far as possible.
- f. Additional guidelines for manual sampling:
 - (1) Sample facing upstream to avoid contamination.
 - (2) Force sampling vessel through the entire cross section of the stream wherever possible.
 - (3) Drop an inverted bucket and jerk line just before impact with the water surface.
 - (4) Be certain that the sampler closes and opens at the proper time when sampling with a depth integrating sampler; with a point sampler, be certain the sampler opens at a proper depth. If doubt exists, discard the sample and re-sample.
- g. When sampling, it is necessary to fill the bottles completely if the samples are to be analyzed for volatile organics, O_2 , CO_2 , NH_3 , H_2S , free chlorine, pH, hardness, SO_2 , NH_4 , Fe^{++} , oil and grease, acidity, or alkalinity. When sampling for bacteria or suspended solids, it is necessary to leave an airspace in the sample container to allow mixing before subsampling.
- h. Collect sufficient volume to allow duplicate analyses and quality assurance testing (split or spiked samples). The required sample volume is a summation of that required for each parameter of interest. Refer to "Methods for Chemical Analyses of Water and Wastewater" (USEPA 1983) for the volume required for analysis of a specific parameter, or the laboratory director for minimum volumes to be collected.
- i. Maintain an up-to-date logbook which notes possible interferences, environmental conditions, and problem areas.
- j. Since the mathematical relationship between volumetric flow and height (or depth) of flow is nonlinear, composite flow proportional samples in relation to the total volume of flow as opposed to gauge height or raw measurement of a secondary device.
- k. If samples are taken from a closed conduit via a valve or faucet arrangement, allow sufficient flushing time to ensure that the sample is representative of the supply, taking into account the diameter, length of the pipe to be flushed, and velocity of the flow.

Ground water

37. Ground-water sampling is much more complicated since a monitoring well samples only a small portion of an aquifer. Unlike surface sampling where a sampling station can easily be relocated, moving a ground-water sampling point implies the installation of additional monitoring wells with all the associated difficulty and expense. Therefore, sampling objectives must be firmly established well in advance of field sampling activities. These sampling objectives will dictate the parameters to be measured, the necessary reliability of the water quality data, and the analytical methodologies which will all determine the sampling procedures necessary to meet the objectives (Scalf et al. 1981; USGS 1977).

38. In assessing pollution of ground water it is essential that water samples be collected in such a manner that will clearly indicate the actual subsurface contaminant concentrations. This may seem to be a relatively simple task; however, it is actually far more complex than most people realize. Some of the more familiar processes which may cause a loss in sample integrity are:

- a. Contamination of the geologic material near the intake zone of the monitoring well.
- b. Contamination by materials used in installation of the monitoring well.
- c. Contamination by sampling materials.
- d. Sample degassing and volatilization.
- e. Contamination from the atmosphere.
- f. Contamination by human factors.

39. Based on studies by Gibb (1981) and others the following recommendations are presented as good techniques to employ in the collection of representative ground-water samples (Barcelona, Gibb, and Miller 1984):

- a. A brief 2- or 3-hr pumping test should be conducted on each monitoring well to be sampled. Analysis of the pump test data and other hydrologic information should be used to determine the frequency at which samples will be collected and the rate and period of time each well should be pumped prior to collecting the sample. If pumping tests cannot be conducted, slug tests may be substituted to provide the needed hydrologic information.
- b. As a general rule of thumb, pumping four to six well volumes will, in most cases, produce samples representative of aquifer water. For aquifers with unusually high transmissivities,

pumping for periods long enough to remove the "stagnant" water column may induce migration of water from parts of the aquifer remote from the monitoring well. The calculations of percent aquifer water with time provide a more rational basis on which the length of pumping can be determined. Samples should be collected in the minimum time required to produce water representative of the aquifer.

- c. A controlled sampling experiment [monitoring indicator parameters (pH, temperature, specific conductance, and Eh) or collecting samples during an extended period of pumping] should be conducted to accurately determine the chemical quality of aquifer water and to verify the response of the monitoring well to pumping, as predicted from the pump test data. This is best accomplished with an in-line closed measurement cell (Garvis and Stuermer 1980). When replicate values of the indicator parameters are observed to vary less than ± 10 percent over three consecutive storage volumes, the well may be presumed to have been adequately flushed for representative sampling. Once the chemical character and response of the monitoring systems have been determined, chemical constituents for routine sampling can be selected.
- d. Based on the sensitivity of the selected chemical parameters, a choice of pumps for routine sampling can be made.
- e. The monitoring wells should be pumped at a constant rate for a period of time that will result in delivery of at least 95 percent aquifer water. The rate and time of pumping should be determined on the basis of the transmissivity of the aquifer, the well diameter, and the results of the sampling experiment.
- f. Measurements of pH, Eh, temperature, and specific conductance also should be made at the time of sample collection. Field determinations of alkalinity, together with a mineral analysis, the foregoing measurements, and total dissolved solids, permit mass and charge balance calculations to be made which are valuable analytical quality control checks.

40. The procedures outlined above are for the collection of representative samples for inorganic analysis. The same procedures will produce representative samples for nonvolatile organic analysis. The use of a syringe sampler (Gillham 1982) in conjunction with a pumping or a bottom-draw bailer has been suggested for collecting ground-water samples for volatile organic constituents.

41. Special care must be taken to prevent cross-contamination when carrying sampling apparatus from one well to another. The sampling devices must be cleaned thoroughly to ensure that contaminants from one well are not carried to the other. Cleaning procedures should be tailored to the analysis of interest. The use of detergents, dilute hydrochloric acid, hexane, and

deionized rinse water often is necessary. In addition, cleaning of sampling devices, all delivery tubes, and tether cables also must be performed thoroughly. The effects of cross-contamination also can be minimized by sampling the least contaminated wells first and progressing to the more contaminated ones. Dedicated sampling devices for each well also may be desirable in certain cases where the potential for cross-contamination is high (Barcelona, Gibb, and Miller 1984).

42. In the case of monitoring wells that will not yield water at a rate adequate to be effectively flushed, different procedures must be followed. There are divergent points of view on how flushing should be performed in these situations. The principal difference in the arguments concerns the degree to which such wells should be evacuated. One suggested procedure includes the removal of water to the top of the screened interval to prevent the exposure of the gravel pack or formation to atmospheric conditions (National Council of the Paper Industry for Air and Stream Improvement (NCASI) 1982). Then the sample is taken at a rate which would not cause rapid draw-down. On the other hand, the wells may be pumped dry and allowed to recover. The samples should be collected as soon as a volume of water sufficient for the intended analytical scheme re-enters the well. Exposure of water entering the well for periods longer than 2 or 3 hr may render samples unsuitable and unrepresentative of water contained within the aquifer system. Finally, in these cases, it may be desirable to collect small volumes of water over a period of time, each time pumping the well dry and allowing it to recover. At present there is very little reliable data on when to choose one sampling method over another in very low yield monitoring wells (Barcelona, Gibb, and Miller 1984).

Sediments

43. Sediment samples can be collected in a number of different ways involving various types of sampling equipment. Plumb (1981) presents an excellent operational evaluation of certain types of grab sediment samplers which may be used by CE samplers.

44. The "National Handbook of Recommended Methods for Water-Data Acquisition" (USGS 1977) presents a thorough explanation of sediment sampling procedures. Included in the presentation are sampling sediments in motion, sampling deposited sediments, sampler types, and sampling procedures for

different sample sources (e.g. lakes, rivers, reservoirs, ponds, estuaries, outfalls).

Field Preparation

45. Sample handling actually covers the time period from when the sample is taken from the environment to final disposition of the sample after analysis. Sampling, sample preparation, and sample analysis are addressed separately in this report. This section will deal with field preparation or the period of sample handling after the sample is taken and before analysis begins. Field preparation topics discussed include sample containers and preservation techniques.

Sample containers

46. There are many variables to consider when choosing proper sample containers. These variables include parameter to be analyzed, durability, resistance to breakage, size, weight, possible interference with analysis components, adsorption and/or desorption tendencies, cost, and availability.

47. Of the two major sample container materials, glass and plastic, borosilicate glass is recommended where glass containers are needed and polyethylene is recommended where plastic containers are used. The literature contains some differing opinions concerning what type of polyethylene to use but the general consensus is to use linear polyethylene first and conventional polyethylene second (American Public Health Association (APHA) 1980; Struempfer 1973; Bately and Gardner 1977; Moody and Lindstrom 1977; Florence 1977). Teflon would be the choice sample container material above polyethylene were it not for the prohibitively high cost.

48. Teflon or polyethylene container caps can be used except where samples are taken in glass for organic (e.g. pesticides, oil and grease, acid extractables, base neutrals, volatiles) analysis. Glass container caps should be made of Teflon or Teflon lined. Aluminum foil cap lining has been used in the past but is not recommended because of its propensity to tear during use.

49. The use of wide mouth sample containers is recommended. Wide mouth containers permit easy sample access and cleaning. The use of narrow neck bottles is only recommended when there is a particular reason to minimize contact with the cap liner or the outside environment.

50. Every laboratory has adopted particular procedures for washing and preparing sample containers. This is fine as long as the absence of contamination from the washing procedure can be documented through an active quality control program using spiked samples, reagent blanks, and sample blanks. The following container washing and preparation procedures are offered as general guidelines for use in CE water quality laboratories (Berg 1982):

- a. Wash containers and caps with a nonphosphate detergent (e.g. Liqui-Nox) and scrub strongly with a brush (if possible wash liners and caps separately).
- b. Rinse with tap water, then distilled water.
- c. Invert to drain and dry.
- d. Visually inspect for any contamination prior to storage.
- e. If the container requires additional cleaning, rinse with a chromic acid solution (35 ml saturated sodium dichromate solution in 1 l of sulfuric acid--this solution can be reused). Then rinse with tap water and distilled water and dry as indicated above.

The analyst should be cautioned that glassware rinsed in chromic acid must be thoroughly rinsed with water to remove all traces of chromium. A commercial product, NOCHROMIX, available from Godax Laboratories, 6 Varick St., New York, NY 10013, may be used in place of chromic acid. Do not rinse plastic bottles in chromic acid.

51. For certain parameters, a special cleaning procedure is needed to avoid adsorption or contamination due to interaction with container walls. These procedures are outlined below:

- a. Metals and phosphorus. If metals are to be analyzed, rinse the container with a solution of one part nitric acid to four parts water, then with distilled water. If phosphorus is to be analyzed, rinse the container with a solution of one part hydrochloric acid to one part water, followed by distilled water. Treat the caps similarly.
- b. Organics. If oil and grease or pesticides are to be analyzed, rinse the sample container with methylene chloride, followed by acetone. For pesticide analysis, use pesticide grade hexane or acetone. The container should have been previously cleaned with chromic acid solution as described previously. Treat the container caps similarly.
- c. Sterilization. For microbiological analyses, sterilize the container and its stopper/cap by autoclaving at 121°C for 15 min or by dry heat at 180°C for 2 hr. Heat-sensitive plastic bottles may be sterilized with ethylene oxide at low temperatures. Wrap bottles in kraft paper or cover with

aluminum foil before sterilization to protect against contamination. An acceptable alternative for emergency or field use is sterilization of containers by boiling in water for 15 min.

52. Containers for specific parameters, as recommended by the USEPA, can be found in Appendix F.

Preservation techniques

53. Preservation methods are limited in their effectiveness and are intended generally to:

- a. Retard biological activity.
- b. Retard hydrolysis of chemical compounds and complexes.
- c. Reduce volatility of constituents.

54. Most of the preservation methods used today are a form of chemical addition, pH control, refrigeration, or freezing. Appendix F contains guidance concerning preservation methods for particular analyses.

55. At its best, sample preservation is very difficult because almost all preservatives exhibit some interferences on particular analyses. Storage at low temperature (4°C) is perhaps the best way to preserve most samples for short time periods (≤ 24 hr). No single method of preservation is entirely satisfactory for water and wastewater, and all methods of preservation may be inadequate when applied to suspended matter (APHA 1980).

56. Particular sampling situations could possibly require alternative preservation procedures from those in Appendix F. The effectiveness of alternate preservation procedures should be demonstrated and documented through simple preservation studies. Such preservation studies should specify:

- a. Type of water/wastewater used as a sample in the experiment.
- b. Type of containers used.
- c. Pretreatment of the container and the glassware used.
- d. Preservation methods used.
- e. Specific temperatures or temperature range used.
- f. Duration of storage.
- g. Stored in light or darkness.
- h. Quality control samples--spikes, duplicates.
- i. Blanks--controls.
- j. Number of samples analyzed, and results.
- k. Statistical analysis, precision, and accuracy.

Sample Shipment

Method of shipment

57. The shipment of environmental samples should be addressed more in terms of common sense than in applying specific guidelines. The idea in sample shipment is to transport the samples to a specific destination in the safest and most expedient manner realistically possible.

58. Certain situations may require that an "overnight" shipper be used. This may be due to a combination of factors such as the perishable nature of the samples and the distance from the sampling site to the analytical laboratory. Most likely the cost of special shipping arrangements will be minimal when compared to the potential cost of the results of bad data from poorly handled samples.

Packing

59. An unacceptable shipping practice is that of packing shipping containers with glass-bottled samples surrounded only by ice. Initially the samples are tight in the container but as the ice melts the bottles hit against one another and breakage almost always occurs. Better packing methods include:

- a. Pack tightly with commercially available frozen packets which retain their volume as they thaw.
- b. Pack tightly with packing material such as foam rubber, styro-foam, and/or plastic materials and then add ice.
- c. Use a combination of a and b above.

Labeling

60. The use of proper sample labeling methods is also important in sample shipment. In some cases samples arrive in a laboratory with labels or tags missing, or with labels or tags illegible because of nonwaterproof ink, and are of no more value than broken samples. It is foolish to spend thousands of dollars to properly collect samples and then lose them in shipment because simple common sense was not applied.

Chain-of-custody

61. Once samples have been collected and appropriate preservation procedures implemented (based on the analytical procedures selected), a conscious effort must be made to ensure that the samples are protected, i.e. are not accidentally mishandled or deliberately tampered with. One of two levels of

protection may be implemented, depending on the use of the data. For normal investigations, a simple chain-of-protection concept can be implemented. In cases where the sample is being collected and analyzed in preparation for possible litigation, more formal chain-of-custody concepts must be implemented.

62. A chain-of-protection procedure is actually nothing more than implementation of good sample collection and laboratory housekeeping practices. Chain-of-protection procedures include such actions as:

- a. The sample is accompanied by the name, mailing address, and telephone number of the sample collector.
- b. The sample is accompanied by the name, mailing address, and telephone number of the laboratory.
- c. There is sufficient quantity of the sample.
- d. The date of shipment is recorded.
- e. A description of the sample is provided.
- f. The sample is packaged so that it does not leak, spill, or vaporize from its packaging.

63. Note that in addition to the above, the shipment of samples must comply with appropriate US Department of Transportation, US Postal Service, or other applicable shipping requirements.

64. When analytical data are to be used in litigation, it is necessary to be able to prove the chain-of-possession or chain-of-custody of any samples from which that data are obtained. It is imperative that each laboratory prepare written procedures to be followed whenever evidence samples are collected, transferred, stored, analyzed, or destroyed. A sample is in custody if it is:

- a. In actual physical possession, or
- b. In view, after being in physical possession, or
- c. In physical possession and locked up so that no one could tamper with it, or
- d. In a designated secure area.

As a minimum, the basic components of a chain-of-custody program include:

- a. A written procedure to ensure that sample possession can be traced.
- b. Appointment of field and laboratory sample custodians and involvement of a minimum number of personnel in sample collection and handling.
- c. Provision of chain-of-custody forms, sample tags, and sample seals.

- d. Ensurance of custody of sample during time it is collected and dispatched to receiving laboratory or turned over to an assigned custodian.
- e. Transfer of possession of individual samples or groups of samples observing transfer-of-custody recording procedures.
- f. Observation of proper laboratory chain-of-custody procedures incorporating a designated sample custodian and a sample storage security area.
- g. Laboratory personnel prepared to testify and show that the sample was in their possession and view or securely locked up at all times from the moment it was received from the custodian until the tests were run.

65. Each laboratory should design chain-of-custody procedures to complement its own particular layout, sample collection, and personnel situation. Detailed information for designing and implementing chain-of-protection and chain-of-custody procedures can be found in the following references:

- a. US Environmental Protection Agency. 1982 (Sep). "Handbook for Sampling and Sample Preservation of Water and Wastewater," EPA-600/4-82-029, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268.
- b. US Environmental Protection Agency. 1982 (Oct). "Manual for the Certification of Laboratories Analyzing Drinking Water," EPA-570/9-82-002, Office of Drinking Water (WH-550), Washington, D.C. 20460.
- c. US Environmental Protection Agency. 1979 (Mar). "Handbook for Analytical Quality Control in Water and Wastewater Laboratories," EPA-600/4-79-019, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268.

PART V: SAMPLE PREPARATION AND ANALYSIS

Background

66. After the sample has been obtained from its point of origin, one or more sample preparation processes may be necessary prior to actual analysis. Sample preparation may involve physical processes such as sieving, crushing, blending, and drying, and/or chemical processes such as dissolution, digestion, extraction, pH adjustment, preservation, and spiking. These physical and chemical processes not only make the analysis job more difficult but are potential sources of contamination and loss of analysis. Therefore, sample preparation should be documented in a very detailed manner so as to provide as complete a sample history as possible. Quality control samples should always be subjected to the identical pretreatment processes as the samples with which they are identified.

Holding Time

67. The holding time of a sample is the time interval between collection and analysis. In general, the shorter the holding time, the more reliable will be the interpretation of the analytical results. Some parameters are so subject to change that it is recommended that they be analyzed immediately in the field (e.g. temperature, pH, chlorine, dissolved oxygen).

68. Guidance concerning holding times for various analyses is found in Appendix F. It is virtually impossible to predict exact holding times which cover all sample types, analyses, and conditions of storage and preservation. Appendix F should be used as guidance, but the habit of performing analysis as quickly as possible after sample collection must continually be cultivated. Where water quality analysis is concerned, procrastination is a mortal enemy and must be guarded against.

69. There are numerous publications containing techniques and procedures for sample pretreatment. The USEPA and APHA publications cover most common pretreatment problems encountered in water quality laboratories. The most popular pretreatment methodology publications, used by the WES Analytical Laboratory Group, follow for reference.

Water:

American Public Health Association. 1980. Standard Methods for the Examination of Water and Wastewater, 15th ed., 1105 18th St., NW, Washington, D.C. 20036.

Skougstad, M. W. 1979. "Methods for Determination of Inorganic Substances in Water and Fluvial Sediments," Techniques of Water Resources Investigation of the U.S. Geological Survey, (200) Un 3t WR, Book 5, Chpt A-1, U.S. Geological Survey.

US Environmental Protection Agency. 1982 (Jul). "Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater," EPA-600/4-82-057, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268.

US Environmental Protection Agency. 1983 (Mar). "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268.

Sediment, tissue, and other complex matrices:

Allen, S. E., Grimshaw, H. M., Parkinson, J. A., and Quarmby, C. 1974. Chemical Analysis of Ecological Materials, Halsted Press, John Wiley and Sons, New York, N.Y.

Black, C. A., et al. eds. 1965. "Methods of Soil Analysis," Parts 1 and 2, Monograph No. 9, American Society of Agronomy, Madison, Wis.

Bock, R. 1979. A Handbook of Decomposition Methods in Analytical Chemistry, International Textbook Co., Bishopbriggs, Glasgow G64 2NZ.

Minczewski, J., Chwastowska, J., and Dybczynski, R. 1982. Separation and Preconcentration Methods in Inorganic Trace Analysis, Halsted Press - John Wiley and Sons, New York, N.Y.

US Army Engineer Waterways Experiment Station. 1981 (May). "Procedures for Handling and Chemical Analysis of Sediment and Water Samples," USEPA/CE 81-1, Environmental Laboratory, Vicksburg, Miss. 39180.

US Environmental Protection Agency. 1982 (July). "Test Methods for Evaluating Solid Wastes," SW-846, Office of Solid Waste and Emergency Response, Washington, D.C. 20460.

US Environmental Protection Agency. "Chemistry Laboratory Manual for Bottom Sediments and Elutriate Testing," EPA 905-4-79-014, NTIS No. PB-294596, Chicago, Ill. 60605.

70. Many other methods references are available and some of the more important ones were listed previously in Part III. These references contain information covering many of the very specific and unique analytical problems encountered in water quality laboratories.

Sample Analysis

71. Sample analysis procedures are presented in the publications which have been previously mentioned. The USEPA, APHA, and American Society for Testing and Materials (ASTM) procedures manuals should be the most useful in determining methodologies to be used in CE water quality laboratories. Appendix F is a list of approved test procedures for specific analyses and a list of specified containers, preservatives, and holding times for those procedures as established by the USEPA (Federal Register 1984). Appendix F procedures will cover most of the normal water quality analyses encountered in CE water quality laboratories. Extreme caution is advised in trying to force these methodologies to conform to every sample brought into the laboratory. There will always be samples with complex matrices which will require special handling methodologies before and/or during analysis. The accepted protocol to be used to modify methods for accepted variances will vary depending on the regulatory agency and the regulatory program (i.e. NPDES, RCRA, CWA, etc). The agency and regulations for each specific program should be consulted for exact protocols.

PART VI: QUALITY ASSURANCE AND QUALITY CONTROL

Background

72. Quality assurance/quality control in chemical analysis is a very old concept. As long as there has been chemical analysis, the need has existed to control the quality of the analysis. There are volumes written concerning the subject of QA/QC. However, regardless of the quantity of literature, if a laboratory does not institute and follow a good day-to-day QA/QC plan, then everything written about QA/QC will have been in vain.

73. There are numerous references (see PART III) with basic "how-to" information concerning design and implementation of QA/QC plans. Therefore, there is really no excuse for any water quality laboratory not to have a written QA/QC plan. Implementation of the plan and dealing with the personalities necessary for implementation (from manager to analyst) are the factors which separate the good laboratory operations from the not so good.

74. This discussion of QA/QC will be concerned with some of the most often disregarded or overlooked QA/QC principles as observed during numerous laboratory inspections by WES Analytical Laboratory Group personnel.

Philosophy of QA/QC

75. Normally the technicians and analysts will exhibit the same attitude toward QA/QC as does management. A positive QA/QC commitment is manifested in numerous ways to include:

- a. Written QA/QC plan and procedures.
- b. Clear statement of objectives by management.
- c. Lines of authority clearly developed.
- d. A QA/QC supervisor with clearly defined authority.
- e. No difficulty in meeting performance requirements.
- f. Good record keeping.
- g. Good workplace atmosphere.
- h. Generally good personnel morale.
- i. Customer satisfaction.
- j. Good data quality reputation.

The right QA/QC philosophy is a must, beginning with the laboratory director or manager and permeating the entire laboratory staff. Quality is not something extra or something nice, it is the foundation of everything done in the water quality laboratory (McCully and Lee 1980).

Factors Affecting QA/QC

Utility service

76. Water supply. One of the most important yet neglected laboratory services is the purified laboratory water (distilled, deionized, etc.). The importance of purified laboratory water is realized in its many uses, e.g., preparation of reagents and standards, dilution of solutions, and final rinsing of glassware. In addition to reagent water blanks being analyzed with all sets of analyses, the laboratory water must be checked periodically (biweekly-monthly). The methods used to check the water may consist of electrical conductivity and resistivity, potassium permanganate (KMnO_4) color retention test, total organic carbon, and others depending upon the analyses being performed. These procedures are all described in the USEPA and ASTM methods manuals previously mentioned.

77. Electrical service. The electrical source coming into a laboratory is never constant unless special equipment has been installed at the source for that purpose. The fluctuations (surges and pulses) of the electrical current, in the form of voltage spikes and noise interference, can cause serious problems with highly sensitive instruments and computer equipment. If the current cannot be regulated coming into the laboratory, then the installation of a voltage surge suppressor and noise filtering device between the AC outlet and the sensitive instrumentation is recommended.

78. Vacuum system. Vacuum sources, whether entire laboratory systems or single vacuum pumps, are often neglected until a malfunction occurs. Periodic service (i.e. clean up, lubricate, change oil, etc.) and installation of moisture traps are a must if trouble-free service and longevity are desired from a vacuum system.

79. Compressed air. Compressed air systems are similar to vacuum systems in that service is required. Compression heats air, increasing its tendency to retain moisture. Compressed air should be filtered coming into the laboratory to eliminate oil, moisture, and other contaminants. Special

filters and/or high-quality compressed air cylinders may be required for use in some laboratory instruments and procedures.

80. Fume hoods. Chemical fume hoods are a very necessary part of a good water quality laboratory. Regular fume hoods should have a velocity of 100 lin ft/min with the sash fully open (USEPA 1979). Special hoods with washdown systems are necessary when performing perchloric acid digestions. The height and proximity of a hood's exhaust stack to the air intake source for the laboratory and other hoods are critical factors and can be a serious source of contamination. This is an important consideration in the installation of new fume hoods. Fume hoods should generally not be located near door openings, near windows, or along principal traffic lanes. All of these locations can cause considerable fluctuations in the air velocity of the hood and are possible sources of contamination to the air entering the hood.

Instrumentation

81. Selection. There are many factors involved in selecting analytical instrumentation, some of which include:

- a. Level of measurement desired.
- b. History of downtime.
- c. History of service quality.
- d. Laboratory size
- e. Installation.
- f. Cost.
- g. Performance record in other laboratories.
- h. Personal preference.

These factors differ from laboratory to laboratory; therefore, any guidance would have to be tailored to a specific laboratory situation.

82. Calibration. Regardless of the instrument and equipment types, a system of calibration and preventive maintenance is necessary. The QA/QC plan should specify maintenance requirements and schedules, and the regular maintenance should be documented upon completion.

83. A typical example of equipment neglect is the analytical balance, which is probably the most important piece of equipment in the laboratory. It is recommended that all balances be serviced by a qualified service man at least every 4 to 6 months. Standardized weights, traceable to the National

Bureau of Standards, should be available and in use on a daily basis to continually check the operation of the balance.

84. All laboratory instruments need periodic servicing and calibration. In Table 9 the USEPA (1978) gives calibration recommendations for some of the major laboratory instruments. These "recommendations" are not to be considered rigid rules but should give the laboratory manager an idea of what type of service is needed and approximately how often it is needed. The manager can use these recommendations and develop a schedule for inclusion into the laboratory QA/QC plan.

Glassware and lab tubing

85. Errors in analysis due to glassware and laboratory tubing can be realized in several ways. Contaminated or dirty glassware can cause serious analysis errors, especially in trace analysis. The method of cleaning (discussed previously) must be commensurate with the contaminants being removed and the level of analysis being performed. It is often necessary to reserve special glassware just for a specific analysis (e.g. specific metals, phosphorus, etc.). It is good laboratory technique to rinse glassware with tap water or organic solvent and again with water as soon as possible after use. Contaminants allowed to dry on glassware are much more difficult to remove. Lab tubing has also been shown to be a common source of contamination (i.e. plastic-phthalate esters, rubber-zinc).

86. A common problem observed among many laboratories is the use of old, etched, chipped, and/or cracked glassware. This is a dangerous practice because etched or cracked glassware will more easily adsorb contaminants or the constituent being analyzed. In either case false results can and most likely will occur. When a bottle brush is used to clean glassware, be sure there are no exposed metal edges or points which might scratch the glassware.

87. For volumetric analysis, Class A volumetric glassware must be used. The precision of volumetric work depends on the accuracy with which volumes of solutions can be measured. Proper technique in handling volumetric glassware must be used and taught to new analysts. Volumetric measurements must be made at constant temperatures. Volumetric delivery systems must be read correctly. Read correctly means that the bottom of the meniscus should be tangent to the calibration mark on the volumetric apparatus with the eye and the graduation mark on the same horizontal plane. If the meniscus is not read in the proper plane, a type of error will result called parallax (Clark 1980). If the eye

Table 9
Instrument Calibrations*

Instrument	Procedure	Frequency
Analytical balances	Zero	Before each use
	Standard weights	Monthly
	Full calibration and adjustment	Annually
pH meters	At pH 4, 7, and 10	Daily
Conductivity meters	Obtain cell constant with potassium chloride reference solutions	Daily
	Construct temperature curve if measurements are to be made other than at $25 \pm 0.5^{\circ}\text{C}$	Monthly
Nephelometer/ turbidimeters	Check instrument scales or develop calibration curve with formazine stds. (≤ 4 NTU)	Monthly
	If manufacturer's stds. are not formazine, check against formazine stds. (≤ 4 NTU)	Annually
Colorimeters/filter photometers	Curves determined with five to six laboratory-prepared std. solutions for each parameter in conc. range of samples	Daily
UV/visible spectrophotometers	Wavelength calibration with helium oxide glass or solution, low-pressure mercury arc, benzene vapor (UV), or hydrogen arc (visible)	Quarterly
	Absorbance vs. concentration curves with five to six std. solutions for each parameter at analytical wavelength in conc. range of samples	Daily
	Full servicing and adjustment	Annually

(Continued)

* Source: USEPA (1978).

Table 9 (Continued)

Instrument	Procedure	Frequency
Infrared spectro- photometers	Wavelength calibration with polystyrene or indene	Daily
	Absorbance vs. concentration curves with five to six std. solutions for each parameter at analytical wavelength in conc. range of samples	Daily
	Full servicing and adjustment	Semiannually
Atomic absorption spectrophotometers	Response vs. concentration curves with six to eight std. solutions for each metal (std. mixtures are acceptable, but with same acid as samples to be run) in conc. range of samples	Daily
	Full servicing and adjustment	Annually
Carbon analyzers	Curves determined with five to six std. solutions in conc. range of samples	Daily
DO meters	Calibrate against modified Winkler method on aerated distilled or tap water	Daily
Other selective ion electrodes and electrometers	Curves determined with five to six std. solutions in conc. range of samples	Daily
Thermometers	Calibrate in constant temperature baths at two temperatures against precision thermometers certified by National Bureau of Standards	Quarterly
Technicon auto analyzer	Curves determined with std. solutions for each parameter	Each set of samples
	Full service and adjustment (esp. colorimeter)	Annually

(Continued)

(Sheet 2 of 5)

Table 9 (Continued)

Instrument	Procedure	Frequency
Gas chromatographs	Retention times and detector response checked with std. solutions	Daily
	Response curves for each parameter determined with std. solutions	Monthly
Radiological equipment	(See <u>Standard Methods</u> , Sect. 300)	
Sulfur dioxide in air sampler/analyzers (pararosaniline method)	Calibrate flowmeters and hypodermic needle against a wet test meter	Quarterly (needles before and after each run)
	Spectrophotometric calibration curve with five to six std. sulfite-TCM* solutions at controlled temperature ($\pm 1^\circ\text{C}$)	Monthly
	Sampling calibration curve with five to six std. atmospheres from permeation tubes or cylinders	Monthly
	Calibrate associated thermometers, barometers, and spectrophotometer (wavelength)	Quarterly
	Calibrate sampler (curve of true airflow rate vs. rotameter or recorder reading) with orifice calibration unit and differential manometer at six air flow rates.	Monthly
Suspended particulates (high-volume sampler method)	Calibrate orifice calibration unit with positive displacement primary standard and differential manometers	Annually
	Calibrate relative humidity indicator in the conditioning environment against wet-bulb/dry-bulb psychrometer	Semiannually
	Check elapsed time indicator	Semiannually
	Calibrate associated analytical balances, thermometers, barometers	As needed

(Continued)

* TCM = potassium tetrachloromercurate.

(Sheet 3 of 5)

Table 9 (Continued)

Instrument	Procedure	Frequency
Carbon monoxide (nondispersive IR)	Determine linearity of detector response (calibration curve) with calibration gases (0, 10, 20, 40, and 80% of full scale, certified to $\pm 2\%$ and checked against auditing gases certified to $\pm 1\%$)	Monthly
	Perform zero and span calibrations	Daily or every 3 days
	Calibrate rotameter and sample cell pressure gauge	Semiannually
Photochemical oxidants (ozone)	Calibrate standard KI/I ₂ solutions in terms of calculated O ₃ equivalents at 352 nm	At same time as ozone generator
	Calibrate instrument response with six to eight test atmospheres from ozone generator, spanning expected ranges of sample concentrations (usually 0.05-0.5 ppm O ₃)	Monthly
	Calibrate flowmeters, barometer, thermometer	Semiannually
	Calibrate and service spectrophotometer	As specified
	Calibrate ozone generator	Monthly
Hydrocarbons (corrected for methane)	Determine linearity of detector response (calibration curve) with calibration gases (0, 10, 20, 40, and 80% of full scale, certified to $\pm 2\%$ and checked against auditing gases certified to $\pm 1\%$)	Monthly
	Perform zero and span calibrations	Before and after each sampling period
	Calibrate flowmeters and other associated apparatus	Semiannually

(Continued)

(Sheet 4 of 5)

Table 9 (Concluded)

Instrument	Procedure	Frequency
Nitrogen dioxide (arsenite 24-hr sampling method)	Calibrate flowmeter with wet test meter	Monthly
	Calibrate hypodermic needle (flow restrictor) with flowmeter	Each new needle and before and after each run
	Obtain colorimetric calibra- tion curves with five to six std. nitrite solutions	Weekly
Nitrogen dioxide (chemiluminescence, continuous)	Determine linearity of detec- tor response (calibration curve) with calibration gases (0, 10, 20, 40, and 80% of full scale, certified to $\pm 2\%$ and checked against auditing gases certified to $\pm 1\%$)	Monthly
	Perform zero and span calibrations	Daily or every 3 days
	Calibrate rotameter and sample cell pressure gauge	Semiannually
Autoclaves and sterilizers	Check sterilization effectiveness (e.g., <i>B. stearothermophilus</i> , color-indicator tape for ethylene oxide)	Daily
	Calibrate temperature-recording device	Semiannually

(Sheet 5 of 5)

is above the plane of the meniscus and looking downward, the meniscus will appear higher and result in a high reading with the opposite being true if the eye is below the meniscus. To avoid parallax, line up the bottom of the meniscus with the graduation mark where it appears both in front of the container and where it extends around to the other side.

88. Thorough discussions of laboratory glassware can be found in previously referenced publications by the USEPA, APHA, and ASTM (e.g. 15th Edition of Standard Methods (APHA 1980), "Handbook of Analytical Quality Control for Water and Wastewater Laboratories" (USEPA 1979), Annual Book of ASTM Standards - Section 14 (ASTM 1983b)).

Reagent purity

89. The purity of laboratory reagents is of considerable concern. It is recommended that Analytical Reagent Grade chemicals be used as a minimum in CE water quality laboratories. Specialized tests may require higher degrees of purity (i.e. trace metals). An analyst must analyze a reagent blank with every group of analyses to keep a constant check on the background levels of the reagents. Reagent blanks should also be analyzed before any sample preparations are performed such as acid digestions and extractions. This can save a lot of time and effort if a contaminated reagent is found.

90. It is recommended that reagents be dated and properly stored as they are received and/or made. Periodic inventories and proper disposition of old reagents should be made. These procedures should be detailed in the laboratory QA/QC plan.

Data management

91. Precision and accuracy. As noted in Part III there are numerous references concerning laboratory QA/QC and most of these references deal extensively with the concepts and statistics associated with precision and accuracy. For a more thorough discussion of the concepts of accuracy and precision, refer to the Part III publications. Only practical applications of precision and accuracy and related terms will be considered in this discussion.

92. In observing many analytical water quality laboratories over the years, the greatest precision and accuracy shortcoming is documentation. Most of the laboratories observed were performing accuracy and precision operations (e.g. spikes, duplicates, Standard Reference Material (SRM's), etc.) but the documentation of these operations was either incomplete or nonexistent.

Documentation of accuracy and precision data not only includes an easily recognizable presentation of the data but it should also include statistical expansion of the data (e.g. percent recovery, coefficient of variation, standard deviations, control charts, etc.).

93. Control charts. The lack of or inconsistent use of control charts is an area observed to be lacking in a lot of water quality laboratories. This is very unfortunate considering the amount of information one may obtain by just glancing at a properly constructed control chart.

94. Interpretation of control charts requires the use of certain rules or decision points which must be followed in order to judge a measurement process out of control. Examples of these rules might be:

- a. One or more points outside three standard deviations.
- b. Two or more consecutive points outside two standard deviations.
- c. A run of four points outside one standard deviation.
- d. A run of seven or more points (this may be either seven consecutive points above or below the mean or seven consecutive points increasing or decreasing).

It is better to use a combination of rules such as the four above than a single rule. All such rules and procedures should be outlined in the laboratory QA/QC plan.

95. Many analytical problems can be detected in their early stages by the use of control charts. The basic symptoms seen on the control charts are either a shift or trend. Some of the more common causes of these symptoms are:

<u>Symptom</u>	<u>Common Cause of Symptom</u>
Shift in mean	Incorrect preparation of standard Incorrect preparation of reagents Contamination of sample Incorrect instrument calibration Analyst error
Trend of mean upward	Deterioration of standard Deterioration of reagents
Trend of mean downward	Concentration of standard due to evaporation of solvent Deterioration of reagents
Increase in variability	Poor analyst performance, e.g., poor technique, lack of training, deviation from procedure

96. No matter how much individual or group effort an analyst or laboratory staff puts into steps to ensure accuracy and precision, if one of those steps is not thorough documentation, then all other steps are in vain.

97. Records. Records are extremely important in permitting a water quality laboratory to provide a quality product. Good record systems will:

- a. Establish and maintain chain-of-custody.
- b. Identify an item.
- c. Describe the analytical procedure.
- d. Report the results of the analysis.
- e. Provide documentary proof of the processing of a sample.
- f. Document the accuracy and precision of the data.

98. Proper written documentation is an essential key to good QA/QC practices in a water quality laboratory. It is evident that poor record keeping practices can have a serious adverse impact on a laboratory's ability to properly accomplish its mission. Without proper records, the factual information necessary to make and/or defend a decision may not be available.

QA/QC Summary

99. Water quality laboratories must plan, write, and implement an integrated program, involving the entire staff, for QA/QC. The QA/QC program establishes a standard of quality, procedures to meet that standard, control points to measure the effectiveness of the procedures, correction and feedback mechanisms, and audits to evaluate the entire program. Only through such a QA/QC plan can the level of quality of a laboratory's information be controlled or judged acceptable.

100. The following are a few quality assurance axioms (McCully and Lee 1980) worth repeating and worth remembering:

- a. Everyone must be actively involved with quality every day. Quality assurance is not something special done once a quarter but must be done every day on every sample.
- b. Don't make assumptions - check everything.
- c. You (the analyst) are responsible for what you do (not management, not your supervisor, etc.).

- d. Keep records (you really won't remember and even if you do, you will have moved). All relevant quality data and checks must be recorded.
- e. Quality isn't something extra or something nice, it is the foundation of everything we do.
- f. Bad data are worse than no data.
- g. Nothing is perfect. Be aware of the limits, i.e., how good (bad) are the reagents, methods, data. Don't keep it to yourself, make everyone else aware of the limits as well.
- h. Opinions are worthless - where are the data?
- i. Quality problems are not fate. They have causes and can be corrected.

PART VII: POTENTIAL PROBLEMS WITH COMMON ANALYSES
PERFORMED BY CE LABORATORIES

Background

101. In Part II (Tables 1-4) typical analytical tests performed by the CE water quality laboratories were shown. In this chapter potential analytical problems will be addressed for the methodologies most often used to analyze environmental samples for the constituents mentioned in Part II. A great majority of the potential problems mentioned are a result of direct observation during laboratory inspections.

102. It is understood that the quality of personnel performing the tests may be the largest variable in any procedure. However, for this presentation only the idiosyncrasies of the particular analytical methodology will be discussed (e.g. interferences, matrix, reagent, instrument, and pretreatment problems, etc.). Unless otherwise stated, most of the analytical procedures will be those shown in Appendix F.

Color

103. Color in water is caused by the presence of metallic salts, organic matter, and other dissolved or suspended materials. An arbitrary standard for color has been set up using a platinum-cobalt solution where one unit of color is equal to 1 mg/l of platinum.

104. Normally the Visual Comparison Method or Spectrophotometric Method (204 A. and 204 B. of Standard Methods (APHA 1980)) is used in water quality laboratories. For some purposes a method developed by the American Dye Manufacturers Institute (ADMI) may be useful (204 D. of Standard Methods (APHA 1980)). Although more complex than the first two methods, the ADMI method is useful where unusual hues are encountered (e.g. some industrial wastewaters).

105. Color may be expressed as "apparent" or "true" color. Apparent color includes that from dissolved and colloidal materials plus that from suspended matter (turbidity). By filtering or centrifuging out the turbidity, true color can be determined. Generally, only the true color value is determined in water quality laboratories. If apparent color is requested, it can be determined by measuring an untreated water sample.

106. Some of the most often observed problems related to color analysis include:

- a. Incomplete turbidity removal causes the apparent color to be noticeably higher than the true color. This problem occurs most often when only centrifugation is used for turbidity removal. Centrifugation is acceptable only if turbidity removal equivalent to filtration is achieved (APHA 1980). For highly turbid samples a combination of centrifugation and filtration is best in order to avoid filter clogging.
- b. The pH at which color is determined must be specified. Color is very pH-sensitive and normally increases as pH increases (APHA 1980).
- c. When color samples are taken, make sure they are refrigerated at 4°C.
- d. Analysts must be checked against color standards. Color blindness may rule out the use of the visual comparison method for certain analysts.

Specific Conductance

107. Modern specific conductance cells have a characteristic electrode spacing/area ratio known as the "cell constant." The cell constant (K) is a factor which is used to determine the specific conductivity range (micromhos per centimetre) of that particular cell. It is determined by the physical configuration of the cell and the electrodes. Cells with constants of 1.0 or greater normally have small, widely spaced electrodes, while cells with constants of 0.1 or less have large electrodes which are closely spaced. Generally, cells with $K = 1.0$ should be used for solutions with conductivities of more than 20 $\mu\text{mhos/cm}$. Cells with $K = 0.1$ should be used for solutions with conductivities less than 20 $\mu\text{mhos/cm}$.

108. Some of the most often observed problems related to specific conductivity analysis include:

- a. Use of the wrong cell constant (K) for the specific conductance range in question can cause serious errors.
- b. Calibration of the conductivity cell must be performed and checked periodically. A calibration constant is a factor by which scale readings must be multiplied to compute specific conductance.

$$K_{sp} = cM \quad (1)$$

where

K_{sp} = actual specific conductance

c = calibration constant
M = meter reading

For example, a 0.001 N KCl solution (147 μ mhos/cm standard) may show a scale reading of 147.

$$147 = c \ 147, \ c = \frac{147}{147} = 1.00$$

In this case the cell is perfectly "matched" to the instrument, the calibration constant is 1.00, and the scale reading represents actual specific conductance. A variety of cells, each covering a specific range, may be used with any one instrument. However, a calibration constant for each cell must be computed before solutions of unknown specific conductance can be determined (USEPA 1981). The above equation assumes that all samples are at 25°C before the conductivity is measured. Conductivity increases about 2 percent per degree Centigrade, so be sure that all samples are at 25°C before measuring them. The magnitude of the increase depends upon the exact ionic constituents in the samples, so the correction usually is unreliable (Carson 1978).

- c. Some samples can affect the platinized surface of the cell and thus affect the cell constant and measured results. Measure the conductivity of the 0.01 M KCl solution at least daily and after any sample that is strongly alkaline or acidic or containing grease and oil or organic solvents. Any variation of more than 1 percent from the standard value of 1413 μ mhos/cm at 25°C is cause for re-platinizing the cell electrodes. Standard Methods (APHA 1980) describes the platinizing procedure. Re-standardize after re-platinizing (Carson 1978).
- d. There is a slight nonlinear response of conductance with increasing salt concentration, the magnitude of which depends upon the specific ionic constituents. For example, 0.0001, 0.001, 0.01, 0.1, and 1 M KCl solutions have conductances of 14.94, 147.0, 1413, 12,900, and 111,900 μ mhos/cm, respectively. If the conductance of a sample is out of range of an instrument, the value determined by dilution will be from 5 to 15 percent too high. Determine the range of acceptable accuracy for a particular instrument by measuring the conductance of the above molar solutions. An error of less than 1 percent at any concentration is normally acceptable (Carson 1978).
- e. The single most important requirement for accurate and reproducible results in conductivity measurement is a clean cell. A contaminated cell will contaminate the solution causing the solution conductivity to change. Clean cells as follows:
 - (1) Prepare a solution containing 100 ml isopropyl alcohol, 100 ml ethyl ether, 50 ml concentrated HCl, and 50 ml distilled water.

CAUTION: Ingredients are extremely flammable and caustic. Observe proper safety precautions, including rubberized skin protection, safety glasses, no spark or flame within 50 ft, and good ventilation.

- (2) Dip the cell into the solution, making certain it is submerged beyond the vent slots in the electrode chamber.
- (3) Agitate the solution for 1 to 2 min.
- (4) Remove the cell from the solution and rinse it in several changes of distilled water. Inspect the platinum black to see if re-platinizing may be required.

pH

109. The measurement of pH is one of the most common analytical techniques used in water quality laboratories. Due to the commonality of pH, the actual measurement and measurement equipment is often taken for granted, hence the pH measurements made often suffer from the effects of incorrect materials or incorrect maintenance.

110. A pH measurement system consists of four parts: a pH-sensing electrode, an amplifier which translates a voltage response into something the user can read, a reference electrode, and a sample. Each component of the system plays a critical role in the measurement process.

111. When problems arise in pH measurement, the source of the problem is typically the reference electrode. Some manufacturers report that up to 70 percent of the pH measurement problems are traced to reference electrode problems (Fisher 1984). It stands to reason, therefore, that a check of the reference electrode would be the place to start in troubleshooting pH measurement problems.

112. The first indication of reference electrode problems is usually a very long stabilization time. Long stabilization times can also be caused by temperature changes, solution reactions, or atmospheric CO₂ absorption. Generally, however, the long stabilization time is caused by incompatibility of sample and reference electrode or by a faulty reference electrode.

113. Some simple methods for checking the performance of a reference electrode include:

- a. Move your hand quickly toward and then away from the electrode. If the pH meter reading changes in response to the hand movement then a faulty reference electrode may be suspected.

- b. If stirring causes instability then turn the stirrer off. If significant changes in pH readings occur, then reference electrode problems may be assumed.
- c. If stirring causes noise (reading variation) and reducing the stirring speed reduces the noise, then suspect reference electrode problems.
- d. If other electrodes are available, switch them for the suspect electrodes. A cleaning procedure may then be used to see if performance can be improved for the faulty electrode. There are many different rejuvenation procedures for electrodes and the manufacturer's recommendations should be followed for specific electrodes.

114. For periods of time up to 48 hr, it is best to store combination electrodes (glass and reference electrodes in a single probe) in air, with a protective cap over the end of the electrode and the filling hole covered. For long-term storage (>48 hr), it is best to remove the filling solution and store the electrode completely dry.

115. Gel-filled combination electrodes should never be left stored in any solution for long periods of time. Sample solution will migrate into the diffusion type electrode (gel) and cause long stabilization times. Wet storage of gel-filled electrodes can cut their useful life to a tenth of what might be ordinarily expected.

116. The operation of a pH meter is simple and often taken for granted. In every case follow manufacturer's instructions for specific pH meters and for storage and preparation of electrodes for use. A few simple checks can help ensure the proper performance of a pH meter:

- a. Check calibration. Prepare or obtain pH buffers covering the range of interest, usually pH 4 (potassium hydrogen phthalate), pH 7 (potassium and sodium phosphate), pH 9 (sodium borate). Make sure all solutions are at room temperature and set the temperature response knob on the meter to that value.
- b. Immerse the electrode(s) in the pH 7 buffer and adjust the meter to read 7 with the calibration adjust knob. Rinse the electrodes well with distilled water, wipe dry with a lab tissue, and immerse in different buffer. The measured value of the second buffer should agree within 0.1 pH unit of the stated value for good quality electrodes.
- c. If problems occur, check the electrolyte level in the reference electrode, the porous plug in the reference electrode, to be sure it is not plugged and the glass membrane of the

measuring electrode to be sure it is not coated with dirt or grease and is not scratched. Most problems can be traced to faulty electrodes. Replace electrodes if necessary to achieve proper performance.

- d. Some pH meters have a slope adjustment to correct for a non-linear electrode response. If available, set the proper pH value of the second buffer with the slope adjustment.
- e. Correct drift. The pH reading for nonbuffered samples will not stabilize as fast as with highly buffered solutions. Place the electrodes in a typical water sample after the meter has been standardized. Turn the meter on and observe the pH reading. It should stabilize in 30 to 60 sec. If not, check the electrodes for proper performance as previously mentioned.

117. Newer model pH meters may perform various functions automatically (i.e. temperature compensation, buffering, etc). It is still necessary, however, to make sure that the electrodes are in good repair and functioning properly.

Solids (Residue)

118. All of the tests for solids are gravimetric. Because there are so many variables, total solids and the various portions of solids are most practically defined in terms of the test conditions used for their determination. Using the term "residue" emphasizes that the data obtained is for matter which remains after applying treatments specified by a standard test procedure.

119. Some of the interferences and sources of error associated with solids analysis are listed below:

- a. Normally, nonrepresentative particulates such as leaves and sticks are removed from the sample before processing.
- b. Floating oil and grease should be included in the sample and dispersed by a blending device before taking an aliquot for analysis.
- c. If evaporation of total and/or dissolved (filterable) solids is conducted in a drying oven, lower the temperature to 98°C to prevent boiling and spattering of the sample.
- d. Negative error is possible due to loss of volatile materials during evaporation.
- e. Use tongs or weighing gloves to handle crucibles and evaporating dishes because fingerprints can result in weighing errors.
- f. Hygroscopic components (e.g. Ca^{+2} , Mg^{+2} , Cl^{-1} , SO_4^{-2}) require prolonged drying and desiccation, followed by rapid weighing.

- g. Bicarbonate component requires careful and prolonged drying to ensure conversion to carbonate.
- h. Take every possible precaution to obtain a representative sample.

120. It is important to remember that due to the nature of the tests, residue analysis does not yield extremely accurate results. Consistent technique in carrying out the steps of the test as specified can control procedural variables and increase the quality of the data.

Turbidity

121. Turbidity measurements represent the optical property of light scattering by suspended solids. The nephelometer is the generally accepted means by which turbidity is measured. Likewise, the preferred expression of turbidity is in nephelometric turbidity units (NTU). Basically, the nephelometer measures light scattered at a 90-deg angle to the incident light beam and then relates this scattered light to the sample's actual turbidity.

122. The most significant practical consideration in turbidimetric measurement is the difference in measuring turbidity among different instruments that have been calibrated with the same standard material. Differences in the spectral characteristics of the light source/detector combination are the primary reason for different instruments giving different values for the same sample. The authors of Standard Methods (APHA 1980) have attempted to minimize variation by specifying the critical components of an instrument for turbidimetric measurement:

- a. Light source: Tungsten-filament lamp operated at a color temperature between 2,200° and 3,000°K.
- b. Distance traversed by incident light and scattered light within the sample tube: total not to exceed 10 cm.
- c. Angle of light acceptance by detector: centered at 90 deg to the incident path and not to exceed ± 30 deg from 90 deg. The detector and filter system, if used, shall have a spectral peak response between 400 and 600 nm.

The tolerance established by these specifications still allows substantial variability among instruments. Successful correlation of measurements from different turbidity stations can be achieved by using the same instrument model at each station.

123. The greatest misunderstanding in turbidity measurement concerns the natural desire to equate the quantity (milligrams per litre or parts per million) of a sample's suspended material with the sample's measured turbidity. Turbidity is a measurement of the light-scattering properties of a sample's particulates; and, as explained previously, particulate makeup and instrument sensitivity directly affect light scattering and its detection. The analyst must restrict direct correlation of turbidity and quantity of suspended matter to cases where several turbidity measurements are made in succession with the same (or same type of) instruments on samples with the same particulate makeup. Even in these cases many samples do not exhibit a linear relationship between parts per million suspended matter and turbidity value. For example, a natural sample showing a turbidity of 500 NTU often shows a turbidity of substantially more than 100 when diluted 5-to-1 with distilled water. This nonlinear response is due to multiple scattering and greater absorption occurring at the higher concentration.

124. Generally, measurement of turbidity provides an immediate estimate of the relative quantity of suspended solids. For direct suspended solids measurements for each type of turbidity material, turbidity readings must be supported by auxiliary measurements and a correlation (calibration) curve must be established (Hach, Vanous, and Heer 1982).

Acidity and Alkalinity

125. Acidity and alkalinity are simply quantitative measures of a water's capacity to neutralize a strong base or acid to a designated pH. There are numerous references mentioned in previous chapters which will explain fully the principles and theories behind acidity and alkalinity measurements.

126. For the measurement of both of these parameters, the USEPA has recommended the volumetric method with the equivalence point being determined electrometrically (pH meter). The use of a color indicator (methyl orange) is recommended only for the automated method. It should be noted that under National Pollutant Discharge Elimination System (NPDES) requirements, pH meters must be used for the measurement of pH.

127. The pH meter is the primary equipment used in acidity and alkalinity measurements. If the calibration of the pH meter is checked regularly and the suggestions for operation of a pH meter mentioned previously are followed, many possible problems with acidity and alkalinity measurements can be avoided.

128. Other factors to be aware of in acidity and alkalinity determinations include:

- a. Collect samples in clean plastic or glass bottles making sure that the bottles are completely filled and capped tightly.
- b. Avoid excessive agitation or prolonged exposure to air because dissolved gases (e.g. carbon dioxide, hydrogen sulfide, ammonia) can contribute to acidity or alkalinity.
- c. Analyze samples as soon as possible after taking them. Refrigerate samples at 4°C but remember to warm the sample to room temperature before testing.
- d. If samples are filtered (automated analysis), the data cannot be used for NPDES reporting.
- e. For samples containing hydrolyzable metal ions (e.g. ferrous or ferric iron, aluminum, manganese), use the hot peroxide hydrolysis procedure outlined in Standard Methods (APHA 1980). This will eliminate drifting end points caused by slow reaction rates of these metal ions.
- f. In the potentiometric titration, oily matter, suspended solids, precipitates, or other waste matter may coat the glass electrode and cause a sluggish response. Difficulty from this source is likely to be revealed in an erratic titration curve. Do not remove interferences from sample because they may contribute to its acidity. Pause between titrant additions to let electrode come to equilibrium.

Hardness

129. The method normally used to determine hardness is the Ethylenediaminetetraacetic acid (EDTA) titration method. Other than standard laboratory glassware, no special equipment is required for the hardness analysis.

130. Suspended or colloidal organic matter may interfere with the titration end point. This can be eliminated by evaporating the sample to dryness and oxidizing the organic matter in a muffle furnace at 550°C.

131. As outlined in Standard Methods (APHA 1980), inhibitors (e.g. NaCN, MgEDTA) must be used to reduce the interferences caused by certain metal ions. These interferences may appear in the form of fading or indistinct end

points or as pseudo-hardness due to the stoichiometric consumption of EDTA. Table 10 gives some information concerning common interferences in hardness titrations.

132. If the hardness contributed solely by calcium and magnesium is to be determined, then the calculation method (Standard Methods (APHA 1980)) may be used as long as the capability exists to measure the quantities of calcium and magnesium ions present. If the concentrations of soluble metal ions are known, a correction can be made to the total hardness to obtain the hardness contributed by calcium and magnesium only. The hardness contributed per milligram per litre of metal ion is listed below for individual metals. This is a cumbersome way to determine Ca and Mg hardness, and should not be used in preference to the calculation method in Standard Methods (APHA 1980).

<u>Metal (per mg/l)</u>	<u>Hardness Equivalence Factor (mg/l hardness)</u>
Iron	1.792
Aluminum	3.710
Nickel	1.705
Copper	1.575
Cobalt	1.698
Strontium	1.142
Barium	0.729
Zinc	1.531
Manganese	1.822

Chloride

133. The preferred methods for chloride analysis are normally the silver nitrate or mercuric nitrate titrations as outlined in Standard Methods (APHA 1980). The procedures are relatively simple with few complications. Bromide, iodide, and cyanide all titrate as chloride. Oxidation with hydrogen peroxide is necessary to remove interfering sulfur components (e.g. sulfide, sulfite, thiosulfate). In the silver nitrate titration, silver phosphate will precipitate in an excess of 25 mg/l orthophosphate. Chromate and iron in excess of 10 mg/l will also produce interfering effects in both methods.

Table 10

Common Interferences In Hardness Titrations*

Interference	Level	Treatment/Comments
Acidity	No interference up to 2500 mg/l as CaCO_3	For higher levels neutralize sample to pH 7 before running test
Alkalinity	No interference up to 10,000 mg/l as CaCO_3	For higher levels make sample acidic and stir for 2 min (to remove CO_2), then neutralize before running test
Aluminum	No interference up to 0.20 mg/l Al	Add potassium cyanide or add CDTA** Magnesium Salt
Barium	Titrate directly as hardness	Not normally present in greater than trace amounts in fresh waters
Cobalt	Interferes at all levels	Add potassium cyanide or add CDTA Magnesium Salt
Copper	No interference up to 0.10 mg/l Cu	Add potassium cyanide or add CDTA Magnesium Salt
Iron	No interference up to 15 mg/l Fe	Levels up to 30 mg/l give an accurate red-orange to green end point. Potassium cyanide has no effect. Add CDTA Magnesium Salt
Manganese	No interference up to 20 mg/l Mn	Add 0.05 g of hydroxylamine hydrochloride for up to 100 mg/l Mn or add CDTA Magnesium Salt
Nickel	Interferes at all levels	Add potassium cyanide CDTA Magnesium Salt
Phosphate, ortho	Causes early end points	Titrate to a stable blue color which does not reverse to red on standing
Phosphate, poly	Interferes at all levels	Does not occur naturally. Can be converted to orthophosphate by acid pretreatment
Seawater	No interference	Contains high Mg levels and requires a dilution (1:25) or a stronger EDTA titrant (e.g., 0.100 M EDTA)
Sodium	Interferes at saturated levels	Dilute sample or titrate hot

(Continued)

* Hach, Vanous, and Heer (1981).

** CDTA = disodium cyclohexanediaminetetraacetate.

Table 10 (Concluded)

Interference	Level	Treatment/Comments
Strontium	Titrate directly as hardness	Not normally present in greater than trace amounts in fresh water
Temperature	No interference between 2.5° and 95°C	Cold samples should be titrated slowly near the end point. Allow adequate time for the color change to occur
Turbidity	No interference unless end point color change cannot be seen	Ashing is recommended when large amounts of organic matter are present
Zinc	Interferes by causing a slow end point	Add potassium cyanide CDTA Magnesium Salt

134. The automated colorimetric ferricyanide method is another method sometimes used for chloride analysis when the instrumentation is available. Turbid and discolored samples and high suspended solids can cause physical problems in the automated system. Filtration may be necessary and can be done using an in-line continuous filter.

Sulfate

135. The analysis of water samples for sulfate is another relatively simple process. The gravimetric method is subject to interferences causing both high and low results. It is also slow and cumbersome and therefore most water quality laboratories chose the turbidimetric or automated method for sulfate analysis.

136. The main consideration in performing the turbidimetric method for sulfate is timing. From the time barium chloride crystals are added to the sample, the technique must be consistent (i.e. time, mixing speed, dilution, etc.) and the timing the same until a maximum turbidity is obtained. It is critical that all samples, standards, and spikes be treated identically.

137. The main point to remember in the automated methylthymol blue method for sulfate is that the chemistry does not conform to Beer's Law and is not linear. Either an adjustable linearizer must be used or a nonlinear curve must be drawn. Any time a nonlinear curve is used it is a good idea to use more standards (six to eight) than normally used to produce the standard curve. A close watch should also be kept on the ion exchange column. Depending upon the nature of the samples, the ion exchange column may need to be cleaned or replaced more often than with relatively clean samples.

Sulfide

138. Water containing dissolved sulfides readily loses hydrogen sulfide, particularly if the pH of the sample is low. Oxygen destroys sulfides by oxidation, particularly if the pH of the sample is high. Aeration of the sample should, therefore, be avoided. When samples are taken the bottles should be completely filled to eliminate as much air as possible. Addition of zinc acetate and raising the pH above 9 with sodium hydroxide will fix the

sulfide for several days. Acid water must be neutralized before addition of the zinc acetate.

139. Strong reducing agents interfere with both the iodometric and methylene blue procedures. These interferences can be eliminated by first precipitating zinc sulfide, then replacing the supernatant with distilled water. If the procedures outlined in Standard Methods (APHA 1980) are followed closely, most analytical problems with sulfide can be avoided.

Fluoride

140. The principal source of error in fluoride analysis is the presence of interfering ions. This is particularly true of the colorimetric methods. Table 11 lists some ions commonly found in water and their effect on the SPADNS and electrode methods of fluoride analysis.

141. In colorimetric analysis, one of the mechanisms by which these ions cause error is the changing of the reaction rate. Since the determination is based on color development, variations in reaction rate cause variations in fluoride reading.

142. Some ions complex with either fluoride, in all methods, or with zirconium, in the colorimetric methods. When fluoride is complexed, low results are obtained, and when zirconium is complexed, the intensity of color is altered.

143. Chlorine bleaches out the colors of dyes and must always be removed before the sample can be analyzed colorimetrically. Stannous chloride is used to eliminate the chlorine, chromate, and other strong oxidizing agent interferences.

144. If interfering ions cannot be removed or compensated for, the sample must be distilled. Distillation is seldom necessary with the electrode method since it is least affected by interfering ions.

145. Some small but important techniques to remember in the analysis of fluoride include:

- a. The addition of the highly colored SPADNS reagent is critical and should be done with the utmost accuracy. A small error in reagent addition is one of the most prominent sources of error in the SPADNS test.

Table 11
Fluoride Interferences*

<u>Substance</u>	<u>SPADNS</u>	<u>Electrode</u>
Alkalinity	5,000 (-)	7,000 (+)
Aluminum	0.1 (-)**	3.0 (-)
Chloride	7,000 (+)	20,000 (-)
Iron	10 (-)	200 (-)
Hexametaphosphate	1.0 (+)	>50,000
Phosphate	16 (+)	>50,000
Sulfate	200 (+)	50,000 (-)
Chlorine	Must be completely removed with arsenite	>5,000
Color and turbidity	Must be removed or compensated for	--

* Concentration of substance, in milligrams per litre, required to cause an error of ± 0.1 mg/l at 1.0 mg/l fluoride.

** For immediate reading. Allowed to stand 2 hr tolerance is 3.0 mg/l. The 4-hr tolerance is 30 mg/l. After USEPA (1981).

- b. In the automated complexone method, be sure the 8-hydroxyquinoline and subsequent chloroform extraction is performed on samples suspected of containing 0.2 mg/l or more of aluminum.
- c. In the selective ion electrode method ensure that pH 5.0 buffer is added to samples to eliminate interferences due to aluminum, iron, and silicon and other complexes formed at extremes of pH.
- d. If the fluoroborate ion (BF_4) is present the sample must be distilled to hydrolyze the fluoroborate to free fluoride; otherwise the ion selective electrode will not respond to the fluoroborate bound fluoride.

Cyanide

146. Cyanide is normally determined by distillation followed by a silver nitrate titration or colorimetric procedures (barbituric acid or pyridine - pyrazolone methods).

147. The methods detect only simple cyanides, and it is therefore necessary to break down any complex cyanides present. The decomposition of complex cyanides is normally accomplished by acid reflux or UV digestion followed by distillation.

148. Common interferences include sulfide, heavy-metal ions, fatty acids, steam-distillable organic compounds, cyanate, thiocyanate, glycine, urea, oxidizing agents, and substances which may contribute color or turbidity to the sample. These interferences may be removed or their effect mitigated as follows:

- a. Sulfide is removed as lead sulfide by adding a slight excess of lead carbonate to 400 ml of the alkaline (pH 11.0 or above) sample. Filter the sample immediately, wash the precipitate, and add the washing to the filtrate.
- b. Fatty acids are removed by acidifying 400 ml of sample with acetic acid to a pH between 6 and 7 and extracting with 80 ml of either isooctane or hexane. A single extraction is usually sufficient.
- c. Oxidizing agents are removed by adding sodium sulfite or sodium arsenite until a negative test with starch-iodide paper is obtained.
- d. Most remaining interferences are removed by the distillation. Standard Methods (APHA 1980) and Annual Book of ASTM Standards - Section 11 (ASTM 1983a) have good sections on

troubleshooting the various interferences associated with cyanide analysis.

149. Extreme caution must be exercised in the analysis of cyanide due to its toxic nature. However, many laboratories have been observed performing cyanide analyses outside of a hood. Do not take this analysis for granted as far as safety is concerned.

Metals

150. There is a vast quantity of literature available which addresses the problems and solutions involved in the analysis of metals by atomic absorption spectrophotometry (AAS). A repetition of information available in USEPA (1983) and APHA (1980) will be avoided; however, a review of the major types of interferences will be helpful. The major AAS interferences include ionization effects, chemical effects, matrix effects, spectral line effects, and background absorption.

Ionization effects

151. If a significant number of the atoms of the element being determined become ionized in the flame, an error in the analysis will result. This ionization is due to excessive flame temperature, which may be altered to control this interference. Another type of interference may be caused by the presence in the sample of other, more easily ionizable elements than the one sought. The signal enhancement which results may be controlled by the addition of a sufficient amount of the interfering element to both sample and standards to produce a "plateau" in the absorbance curve, above which no further increase occurs.

Chemical effects

152. This type of interference is due to the formation, in the flame, of compounds of the element sought which are difficult to decompose, thus reducing the amount of the element available for absorption. The formation of such compounds may often be precluded by the addition of another element, such as lanthanum, which forms a less-soluble salt with the interfering anion than does the element desired. The interfering anion is thus effectively reduced in concentration in the flame, and the interference is minimized. A modification of the fuel-to-oxidant ratio of the flame as well as the choice of fuel and oxidant can also be used to reduce this type of interference.

Matrix effects

153. Unequal amounts of dissolved solids in samples and standards may cause errors in the analysis due to different nebulization of such solutions by the atomizer. This may usually be controlled by matching the density or viscosity of samples and standards, or by adding a noninterfering salt to the standards. Usually, if matrix effects are severe, the standard addition technique is used.

Spectral line effects

154. Spectral line interference is not commonly encountered. It occurs when there is overlap of a spectral line of the element sought and that of another element that is present in the test sample. Usually, sufficiently high resolution of the spectrometer precludes these problems. However, when a nonanalyte element is present at very high concentration, its atomic line becomes broadened to the extent that it may overlap the line of the sought-for element. The analyst should always be alert to the possibility of errors due to interference of this type.

Background absorption

155. Background absorbance is a collective term used to describe the combined effects of flame absorption, molecular absorption, and "light scattering." It is caused by samples with complex matrices which produce erroneously high analyte absorbance readings. This effect is usually eliminated by the use of background correction such as the deuterium arc (continuum source). Molecular absorption can also often be controlled by using a higher temperature flame with enough energy to break down the absorbing molecular species (USGS 1978).

156. Another method of metals analysis in use in CE water quality laboratories is AAS incorporating a heated graphite furnace. This technique has the advantage of requiring only a very small quantity of sample, and of providing greater sensitivity than flame AAS. Graphite furnaces require longer analysis times and greater operator expertise. Matrix effects may be serious, and it is frequently necessary to use a standard addition method to ensure reliable data.

157. It should be pointed out that with the method of standard additions a minimum of two additions is required, and that each addition should produce a change in absorbance equal to the observed absorbance of the sample.

It is important that the additions show a linear relationship with concentration and that there be no background component to the absorbance of the sample. If either of these premises is violated, the standard-addition method is invalid.

158. As previously stated there are a large number of references available which address the techniques of metal analysis and the methods for overcoming interfering effects. For specific guidance in these areas, references mentioned previously in this report and instrumentation manuals should be examined.

Nitrogens

159. USEPA (1983) contains a good description of possible interferences occurring in the analysis of the various forms of nitrogen. This discussion will identify wrong procedures and errors which can adversely affect the quality of the different forms of nitrogen.

160. Mercuric chloride has been used as an effective preservative for nitrogen; however, its use is now discouraged. The mercury ion interferes with some of the nitrogen tests and also presents a significant disposal problem. Sulfuric acid (pH <2) and refrigeration are combined as the proper preservation techniques for nitrogen forms. Even when properly "preserved," conversion from one nitrogen form to another may occur. Samples should therefore be analyzed as soon as possible.

161. Ammonia samples are easily contaminated by ammonia in the laboratory atmosphere. Any digestion and distillation processes should be performed in a fume hood that is operating properly and that is located in an ammonia-free area of the laboratory. Other laboratory procedures may be performed outside or near this fume hood only if there is no possibility of ammonia contamination.

162. Acid will destroy the cadmium reduction column in the analysis of nitrate-nitrogen. Therefore, samples must either be neutralized or not acid preserved. A buildup of suspended matter in the reduction column will restrict the flow. Filtration is recommended to remove suspended material. A preextraction with an organic solvent may be necessary to remove large amounts

of oil and grease. Oil and grease can coat the surface of the cadmium thus decreasing the efficiency of the reduction column.

Phosphorus

163. In addition to the interferences described in Standard Methods (APHA 1980), erroneous results may be obtained due to phosphorus-contaminated glassware and filters. Contaminated glassware is avoided by cleaning it with hot 1:1 HCl, treating it with procedure reagents, and rinsings with distilled water. Preferably this glassware should be used only for the determination of phosphorus and protected from dust during storage.

164. The various forms of phosphorus are defined in Standard Methods (APHA 1980); however, it must be realized that preservation measures only retard the change in these various phosphorus forms. Possible physical changes include solubilization, precipitation, and adsorption on or desorption from suspended matter. Possible chemical changes include reversion of polyphosphates to orthophosphates and decomposition of organic or mineral phosphorus. Possible biological changes include microbial decomposition of organic phosphorus and algal or bacterial growth forming organic phosphorus. One can see from these possible changes that analysis must be performed as soon as possible.

165. The most disregarded sources of phosphorus contamination are glassware and sample handling. If proper care and technique are employed in glassware preparation and sample handling, the standard methodologies should handle most chemical interferences thus making it possible to obtain good, reliable phosphorus data.

BOD, COD, and TOC

166. These tests have probably been the subject of as much controversy as any tests in the water and wastewater field. However, this discussion will bypass any controversy and try to elaborate on some of the procedural pitfalls which may be encountered.

BOD

167. The BOD test is one of the oldest water quality parameters in use today, but it is being used less and less. The time constraints (5-day incubation) and physical handling problems make the BOD less desirable than others from an analyst's point of view. Things to remember when performing the BOD test include:

- a. Analyze samples as soon as possible.
- b. Warm refrigerated samples to 20°C before analysis.
- c. Ensure cleanliness of BOD bottles in order to ensure low blanks.
- d. Run checks on dilution water.
- e. Determine satisfactory seed and ensure its freshness.
- f. Mix dilutions well and make sure enough dilutions are analyzed.
- g. Do not allow air space in bottles.
- h. Ensure a water seal in BOD bottles over entire 5-day incubation period.
- i. Consider invalid any bottles containing entrapped air bubbles after incubation.
- j. Make sure the initial dissolved oxygen of aerated buffered dilution water is greater than or equal to 7.0 mg/l, and preferably greater than or equal to 8.0 mg/l but never greater than saturation value.
- k. Be aware that since there are so many variables, consistent technique will produce good replication better than any other single suggestion.
- l. In data evaluation, be aware of the limitations of the BOD procedure.

COD

168. In the COD test the dichromate reflux method is the preferred analytical method. There are macro and micro versions of the dichromate reflux method and the particular situation and final data use may determine which method is used. As described in Standard Methods (APHA 1980), there are problems with nonoxidation of volatile straight-chain aliphatics and positive interferences exerted by nitrites, ferrous iron, sulfide, and manganous compounds. However, probably the greatest and most common interference is exhibited by chloride. Mercuric sulfate is added to complex chlorides below 1000 mg/l. At higher chloride concentrations a chloride correction curve must be made and applied to the final data. Because of the chloride problems in

the COD analysis, the concentration of chloride should be known for each COD analysis.

169. Special precautions which are advisable for the higher level COD procedure and essential when performing low level COD include:

- a. Keep the apparatus assembled when not in use.
- b. Plug the condenser breather tube with glass wool to minimize dust entrance.
- c. Wipe the upper part of the flask and lower part of the condenser with a wet towel before disassembly to minimize sample contamination.
- d. Steam out the condenser after use for high concentration samples and periodically for regular samples. Use the regular blank reagent mix and heat, without use of condenser water, to clean the apparatus of residual oxidizable components.
- e. Ensure that the distilled water and sulfuric acid are of ^{very} high quality to maintain low blanks for the low level COD procedure.

170. The micro COD method may offer certain advantages (e.g. smaller amounts or reagents, less apparatus, and less space), but the same precautions concerning cleanliness and safety should be observed as for the macro method. In the micro method screw caps with phenolic resin liners are unacceptable since they are attacked by the digestion solution giving erroneously high COD values. Teflon-lined caps greatly reduce this problem, especially if each cap is used only once. Any sample tube which leaks, as evidenced by a black residue on the outside of the tube, should be discarded.

TOC

171. The TOC test is normally performed on carbon analyzers incorporating infrared or flame ionization detection systems. All carbonaceous matter is oxidized and converted to carbon dioxide or methane and detected by infrared or flame ionization, respectively. Points to remember when performing TOC analysis include:

- a. Depending upon the type of carbon analyzer used, the representativeness of the sample taken for introduction into the instrument is very important. Syringes will only accommodate certain size particles and this must be considered in the TOC analysis. Homogeneous samples are a necessity.
- b. Purging of inorganic carbon will cause the loss of certain volatile organics. This must be evaluated for individual samples and recognized when reporting the data.

- c. Instrument operations manuals should be followed closely. Certain types of samples may require a method development effort in order to ensure the reliability of the data.

Summary

172. Table 12 is a comparison of certain parameters relative to the BOD, TOC, and COD tests. Even though TOC may be more precise than either BOD or COD, it does not yield the same kind of information. None of the three tests is a total substitute for the other tests.

Continuous Flow Analysis

173. As noted in the CE water quality laboratory survey, most District and Division laboratories employ continuous flow automatic analyzers (CFAA) in certain colorimetric analyses. Since these analyzers are widespread and in common use, a discussion of various operational hints and techniques will be presented.

174. In building and operating the CFAA system, remember to keep the following in mind:

- a. All tubing should be kept short.
- b. Glass transmission tubing should be kept to a minimum. Aqueous liquids adhere to or "wet" glass, thus increasing sample diffusion.
- c. Appropriate fittings should be used to butt tubing to tubing (N8 and N9 nipple fittings) and tubing to glass (N5 and N6 nipple fittings) connections. Use either 0.110 in. ID sleeving to butt glass to glass, or 1/8- x 1/4-in. heavy wall sleeving. Generally, try to use 1/8- x 1/4-in. sleeving; the thicker wall of the 1/8- x 1/4-in. tubing will protect glass against breakage from shock and will prevent sagging at the butted joints. The 0.110-in. ID sleeving is more often used with the small diameter glass fittings and tubing used with AutoAnalyzer II systems.
- d. All connections should be snug and without spaces in order to avoid breakup of bubbles. Spaces also act like stream eddies, trapping material from previous liquid segments.
- e. A 4-in. stainless steel sample probe with a 0.025-in. ID bore is most often used for delivery rates of more than 2.0 ml/min. A microprobe (0.015 in. ID) is used for delivery rates less than 2.0 ml/min. Sample probes of glass or Teflon are used for acid or caustic samples.

Table 12
Comparison of BOD, TOC, and COD*

Parameter	BOD	TOC	COD
Oxidant used	Bio-oxidation by microorganisms	O ₂ K ₂ Cr ₂ O ₇ K ₂ S ₂ O ₈ Combinations of above plus various catalysts	K ₂ Cr ₂ O ₇ (Others have been used in the past, most notably KMnO ₄)
Time element	5 days	Minutes to hours	2 to 3 hr
Most suitable use	Predicting treatment plant operations and stream loading effects	Measuring total amount of carbon in organic pollutants	Rapid and frequent monitoring of treatment plant efficiency
Accuracy and precision	Not considered highly accurate, +15% standard deviation	± 3-6% standard deviation	Varies, 5-10% standard deviation. May be higher with levels of suspended solids
Advantages	Most closely approximates natural conditions with proper seed	More precise than BOD and COD TOC and COD may be run on same sample for greater information	Correlates with BOD on waste with components of constant composition Change in COD value between influent and effluent may parallel BOD value or supplement BOD Toxic materials do not affect oxidant
Disadvantages	Toxic materials will kill microorganisms Microorganisms do not oxidize all materials present in wastes Inaccuracies with improper seed Length of time required to obtain results	Requires expensive equipment and a highly trained operator for maintenance Some methods may oxidize some pollutants incompletely Measures only total carbon, not oxygen demand potential	Interference from high levels of Cl ⁻ Correlation studies between BOD and COD values must be run Some types of organic compounds are oxidized incompletely

* After Hach, Vanous, and Heer (1984).

- f. The sample line connecting the sample probe with the pump tube should be either polyethylene or Teflon with a 0.025- or 0.015-in. ID. The sample line should be kept as short as possible and its internal diameter should never exceed that of the pump tube.
- g. The sampler wash pump tube should be at least one size larger than the sample pump tube.
- h. Never use a combination of sample and reagent pump tubes that adds up to a diameter less than the diameter of the transmission tubing or improper filling will occur.
- i. Sample cups should be used that are compatible with the sample. Blanks should be analyzed.
- j. Sampler power line should be plugged into a separate circuit from the recorder power line. This will prevent electronic spiking which may occur on the recorder each time the sampler probe is activated.
- k. Pump tubes should be replaced to avoid snaking or side-to-side twisting (generally after about 160 hr of operation).

175. There are certain procedures which can be used to increase the system sensitivity. Some of the best and easiest methods include:

- a. Increase the size or add another delay coil to increase the reaction time for color development (will not help UV methods).
- b. Increase the temperature of the heating bath in 2°C increments until desired or maximum sensitivity is attained. This temperature is normally optimized for specified methods and chemistries.
- c. The quickest and simplest way to increase sensitivity is to increase the flowcell size (path length).
- d. Increase the gain on the recorder and/or the colorimeter. Use caution because baseline noise will also proportionally increase.
- e. Increase the aperture of the sample cell to its maximum.
- f. Decrease the aperture of the reference cell toward its minimum. Exercise caution in decreasing light to the reference detector because poor response and loss of sensitivity will occur after a point (normally beyond 50 percent light reduction). Generally a decrease in reference cell aperture must be accompanied by an increase in the recorder electronic gain.

176. Recorder peak shapes and patterns can give good indications of specific system problems. Table 13 is a listing of some of the symptoms of the most commonly encountered peak distortions and their causes and cures.

Table 13
Symptoms, Causes, and Cures for Irregular CFAA Peak Shapes and Patterns

Symptom	Cause	Cure
Rise curve of peak travels too slowly and does not reach steady-state. Fall curve of peak returns to baseline too rapidly	Rise curve too slow with nonattainment of steady-state. The flowcell pumping rate is too low; hence, slow washout of flowcell. Fall curve returns too rapidly; wash time greater than sample time. The high wash time will not cause inaccuracy, but the time is better spent on sampling rate. On the other hand, the low flowcell pumping rate will cause imprecision if samples fail to reach steady-state.	Increase flow rate through flowcell. Decrease wash time and increase sampling rate.
Peak tailing	Tailing is due to adsorption of either the solute or a reagent (certain reagent dyes like pararosaniline in the sulfur dioxide method) on the inside of the tubing. Severe tailing, if uncorrected, will cause excessive carryover.	Change to a more inert tubing (glass for aqueous streams and Teflon for organic streams). In addition, increase the wash time (decrease sample-to-wash ratio) but do not decrease sample time. Instead, slow down sampling rate and decrease sample-to-wash ratio.
Broad peaks that return to baseline	Although these peaks are acceptable, a considerable amount of time is lost in analysis. The peaks indicate that both the sample and wash time are too great.	Reduce both the sample and the wash time and increase the sampling rate.
Broad peaks that do not return to baseline	The sample time is too large, and/or Flowcell pumping rate is too slow.	Decrease sample time. Although the peaks are acceptable, a considerable amount of time is lost. The wash time is correct. Increase flowcell pumping rate.
Sharp peaks that are not within 95% of steady-state	Sampling rate is too fast and sample time is too short.	Decrease the sampling rate. Increase sample time.
Spurious peaks appearing intermittently during analysis	Air bubbles are passing through the flowcell intermittently.	Check for proper debubbler. Also be sure that the pull-through pump tube flow rate is not too fast. Lower temperature of heating bath. High temperature can cause dissolved gases to be released from stream.
Recorder pen travels off the scale on the strip chart	Air is trapped in the flowcell. Sample concentration is too high.	The trapped air bubbles can be dislodged by squeezing the pull-through line after the flowcell for 10 sec and letting go. Tilt the whole detector so that the outlet of the flowcell is slightly higher than the inlet. If bubbles are repeatedly trapped in the flowcell, check the flowcell for proper positioning and check that the sample pickup line is not aspirating air. Dilute sample and/or decrease colorimeter sensitivity (gain).
There is a sudden shift in the baseline while peaks continue to appear	There is a bubble trapped in the flowcell.	Squeeze any air bubbles out as in the previous problem.
There is cycling of the thermostat in the heating bath (or dialyzer) coupled with incomplete reaction (or dialysis)	There is slow cyclic increase/decrease of peak height when the same sample is tested repeatedly.	Replace the thermoregulator.
There is rapid cycling increase/decrease of peak height when the same sample is tested repeatedly	The sampler cam is defective. Look for a repetitive pattern. For example, if the pattern repeats every three peaks and the center peak of each triplet is high, this indicates that one lobe of a cam having three lobes (a 30 per hour cam) is defective.	Either replace the cam or increase the sample time. If each peak reaches steady-state, defects in the sampler cam will not cause a problem.
An erratic pen movement results in spikes that appear routinely on the strip chart	Switching servo is on the same power line as the sampler.	Plug the power line of the sampler into a separate circuit as a temporary measure. Repair or replace the servo switch.

177. The ideal baseline in continuous flow analysis is free of noise and drift. This is seldom attained, especially in high sensitivity analysis. Therefore, a compromise between the ideal baseline and a sensitive detection system must be reached. A noisy baseline may be caused by:

- a. Incomplete mixing of reagent and sample streams. An extra 5- or 10-turn coil should solve this problem.
- b. Minute air bubbles in the stream (check for turbulence at right angle junctions, keep heating bath temperature below 90°C, check for volatile substances in samples, degas solutions).
- c. Particulates from samples or coated tubing (filter samples or replace tubing).
- d. Incomplete solubilization of reagents.
- e. Oil particles (same as c).
- f. Loose or worn pump tubes.
- g. An empty reagent container.
- h. Incorrect bubble pattern.
- i. Recorder gain too high.
- j. Poor recorder electronics (verify by operating recorder alone).
- k. Defective photocells.

178. Although a baseline drift is occasionally due to a detector and/or recorder malfunction, it is generally due to problems occurring within the analytical stream. A drifting baseline may be caused by:

- a. Slowly deteriorating photocells.
- b. A flowcell that is partially blocked by particles or bubbles.
- c. Coating of the flowcell (adjust pH, clean system, use surfactant).
- d. Schlieren effects (especially with "bottom-to-top" flowcell design), which are caused by changes in the refractive index of the solvents. These are eliminated when a single thickness of translucent tape is placed on one window of the flowcell. This will make the detector less sensitive to Schlieren effects. Back-to-front type flowcells (Technicon Corp.) are designed to eliminate the effects of laminar flow and Schlieren effects.

179. Uneven bubble spacing will cause severe problems, the overall effect being an increase in noise and an erratic baseline and peak shape. The following guidelines may be used to ensure proper bubble patterns:

- a. Use plastic transmission tubing wherever possible. Keep glass transmission tubing as short as possible.

- b. Use surfactants to help prevent the formation of "grease" spots.
- c. Give system a 15-min wash daily with 0.1 N sodium hydroxide followed by a thorough distilled water rinse. The sodium hydroxide helps to make the plastic tubing wettable.
- d. Use crimped plastic tubing and glass tubing with 90-deg bends, which will also break up bubbles.

Priority Pollutants

180. In June 1976 the US District Court Settlement Agreement brought to a conclusion several lawsuits concerning the regulation of toxic discharges. The Settlement Agreement requires the USEPA to investigate and develop control regulations for the discharge into waterways and publicly owned treatment works of "129 priority pollutants," from 21 general point source industrial processes. Bis-chloromethyl ether, dichlorofluoromethane, and trichlorofluoromethane have since been removed from the list leaving 126 toxic pollutants now listed as "priority" toxic pollutants. These pollutants were selected on the basis of their presence in effluents; presence in drinking water or fish; known or suspected carcinogenic, mutagenic, or teratogenic properties; likelihood of human exposure; persistence in the aquatic food chain; tendency for bioaccumulation; and their toxicity to aquatic organisms (Middleditch, Missler, and Hines 1981).

181. There are five major categories of priority pollutants and each category requires different analytical procedures. These categories include the inorganics (Table 14) and four organic groups classified as volatiles (Table 15), base-neutral extractables (Table 16), acid extractables (Table 17), and pesticides (Table 18). The inorganics are detected using AA or ICAP emission techniques. The organics are detected using GC, GC/MS, and/or high pressure liquid chromatography (HPLC) combined with various pre-treatments such as pH adjustments, extraction, and purge and trap.

182. There are many references which address the analysis and identification of priority pollutants. Some very informative and necessary references include:

Middleditch, B. S., Missler, S. R., and Hines, H. B. 1981.
Mass Spectrometry of Priority Pollutants, Plenum Press, New York.

US Environmental Protection Agency. 1977 (Apr). "Sampling and Analysis Procedures for Screening of Industrial Effluents for Priority Pollutants," Effluent Guidelines Division, Washington, DC.

US Environmental Protection Agency. 1980 (Oct). "Interim Methods for the Sampling and Analysis of Priority Pollutants in Sediments and Fish Tissue," Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268.

US Environmental Protection Agency. 1982 (Jul). "Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater," EPA-600/4-82-057, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268.

183. The question may be raised as to why the emphasis on priority pollutants when some of the CE water quality laboratories do not have GC or GC/MS capabilities? No matter where the analyses are completed (in-house or contracted), CE chemists and technicians must be familiar with the analysis procedures and methodologies so that the best data possible may be obtained. With the current emphasis concerning organic pollutants, if the problem has not already surfaced, it is only a matter of time before each Division and/or District Office will be confronted with the problem of priority pollutant analysis and all the various ramifications involved.

184. Since 1976 the so-called "129 priority pollutants" have become a major focus for water quality laboratories. The complexity of analysis, expense, sophisticated equipment, and analyst skill required are all factors which would make priority pollutant analysis of great concern to all CE Districts and Divisions. Due to the magnitude of the complexity of these

Table 14
Inorganic Priority Pollutants*

Antimony	Chromium	Nickel
Arsenic	Copper	Selenium
Asbestos	Cyanide	Silver
Beryllium	Lead	Thallium
Cadmium	Mercury	Zinc

* This category includes salts of each of these substances (except asbestos). Ammonia has also been proposed as a member of this category. After Middleditch, Missler, and Hines (1981).

Table 15
Volatile Priority Pollutants*

Acrolein	1,2-Dichloroethane
Acrylonitrile	1,1-Dichloroethylene
Benzene	<i>trans</i> -1,2-Dichloroethylene
Bis(chloromethyl)ether**	1,2-Dichloropropane
Bromodichloromethane	<i>cis</i> -1,3-Dichloropropene
Bromoform	<i>trans</i> -1,3-Dichloropropene
Bromomethane	Ethylbenzene
Carbon tetrachloride	Methylene chloride
Chlorobenzene	1,1,2,2-Tetrachloroethane
Chloroethane	1,1,2,2-Tetrachloroethene
2-Chloroethyl vinyl ether	Toluene
Chloroform	1,1,1-Trichloroethane
Chloromethane	1,1,2-Trichloroethane
Dibromochloromethane	Trichloroethylene
Dichlorodifluoromethane**	Trichlorofluoromethane**
1,1-Dichloroethane	Vinyl chloride

* After Middleditch, Missler, and Hines (1981).

** Has been deleted.

Table 16

Base-Neutral Extractable Priority Pollutants*

Acenaphthene	Diethyl phthalate
Acenaphthylene	Dimethyl phthalate
Anthracene	2,4-Dinitrotoluene
Benzidine	2,6-Dinitrotoluene
Benzo[<i>a</i>]anthracene	Di- <i>n</i> -octyl phthalate
Benzo[<i>b</i>]fluoranthene	1,2-Diphenylhydrazine
Benzo[<i>k</i>]fluoranthene	Fluoranthene
Benzo[<i>ghi</i>]perylene	Fluorene
Benzo[<i>a</i>]pyrene	Hexachlorobenzene
Bis(2-chloroethoxy)methane	Hexachlorobutadiene
Bis(2-chloroethyl)ether	Hexachlorocyclopentadiene
Bis(2-chloroisopropyl)ether	Hexachloroethane
Bis(2-ethylexyl)phthalate	Indeno[1,2,3- <i>cd</i>]pyrene
4-Bromophenyl phenyl ether	Isophorone
Butyl benzyl phthalate	Naphthalene
2-Chloronaphthalene	Nitrobenzene
4-Chlorophenyl phenyl ether	<i>N</i> -Nitrosodimethylamine
Chrysene	<i>N</i> -Nitrosodiphenylamine
Dibenzo[<i>a,h</i>]anthracene	<i>N</i> -Nitrosodi- <i>n</i> -propylamine
Di- <i>n</i> -butyl phthalate	Phenanthrene
1,2-Dichlorobenzene	Pyrene
1,3-Dichlorobenzene	2,3,7,8-Tetrachlorodibenzo- <i>p</i> -dioxin
1,4-Dichlorobenzene	1,2,4-Trichlorobenzene
3,3'-Dichlorobenzidine	

* After Middleditch, Missler, and Hines (1981).

Table 17
Acid Extractable Priority Pollutants*

<i>p</i> -Chloro- <i>m</i> -cresol	2-Nitrophenol
2-Chlorophenol	4-Nitrophenol
2,4-Dichlorophenol	Pentachlorophenol
2,4-Dimethylphenol	Phenol
4,6-Dinitro- <i>o</i> -cresol	2,4,6-Trichlorophenol
2,4-Dinitrophenol	

* "Total phenols" are also to be measured. After Middleditch, Missler, and Hines (1981).

Table 18
Pesticide Priority Pollutants*

Aldrin	Dieldrin	PCB-1016**
α -BHC	α -Endosulfan	PCB-1221**
β -BHC	β -Endosulfan	PCB-1232**
γ -BHC	Endosulfan sulfate	PCB-1242**
δ -BHC	Endrin	PCB-1248**
Chlordane**	Endrin aldehyde	PCB-1254**
4,4'-DDD	Heptachlor	PCB-1260
4,4'-DDE	Heptachlor epoxide	Toxaphene**
4,4'-DDT		

* After Middleditch, Missler, and Hines (1981).

** These substances are mixtures.

analyses, a comprehensive discussion of priority pollutant analysis is beyond the scope of this report and will follow at a later date. Another reason for addressing priority pollutant analysis techniques at a later date is that not all CE water quality laboratories are at approximately the same level of expertise in this area and not all CE laboratories even have the capability to perform priority pollutant analysis. Even though laboratory expertise or capability does not exist in a particular District or Division, the requirement to perform priority pollutant analysis may very well still exist. If this is the case, then contracting is the obvious answer. Therefore, it behooves all water quality personnel associated with contract management to become very familiar with the priority pollutant analytical procedures even if the personnel never actually perform the analyses. The most current and complete reference for priority pollutant analysis has been previously mentioned but is repeated here for emphasis:

US Environmental Protection Agency. 1982 (Jul). "Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater," EPA-600/4-82-057, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio.

This reference addresses only the organic parameters, which are the major portion. Methods for the 13 metals, cyanide, and asbestos can be found in APHA (1980), USEPA (1983), ASTM (1983a), and Office of Federal Register (1982).

185. Although priority pollutant analysis is relatively new, the future points to the fact that this list will only be expanded. In conversations with USEPA personnel of the Environmental Monitoring and Support Laboratory (EMSL) in Cincinnati, Ohio, they indicate that their work has already expanded to the Hazardous Substances List (Federal Regulation, May 25, 1983) which is a much more comprehensive list than the "126 priority pollutants."* Keep in mind that both lists are proposed regulations, so nothing is legally firm, which is another good reason to address the analysis of toxic organics in a later and separate study.

* Personal Communication, 1984, W. L. Budde, USEPA-EMSL, Cincinnati, Ohio.

PART VIII: SUMMARY AND RECOMMENDATIONS

Summary

186. Chemical analysis may only be a very small portion of the total budget for CE Districts, Divisions, and research laboratories. However, the effects of chemical analysis may pervade every area of CE operations (i.e. planning, construction, and research). It is therefore necessary to ensure that CE water quality personnel are aware of possible pitfalls which may occur in the life of a sample from its inception to final data evaluation.

187. This technical report was oriented to the types of information which could help CE water quality personnel with many of the chemical analysis problems which may be avoided if proper steps are taken. Many sources of potential information were given including government agencies and various written publications. Suggestions were provided concerning USEPA-approved analytical methodologies and recommended QA/QC procedures. Many interferences and troublesome areas in analyses performed by CE laboratories were identified with possible causes and cures. Information was also presented concerning some of the capabilities of CE District, Division, and research laboratories in areas relative to water quality analysis.

Recommendations

188. The necessity for good communication between CE District, Division, and research laboratory water quality personnel cannot be overemphasized.

Therefore, with communication in mind, these recommendations are presented:

- a. Guidance and specifications should be provided concerning contracting for chemical analysis.
- b. Specific guidance and procedures should be written concerning sample handling and preparation techniques.
- c. Guidance concerning organic analysis (especially concerning the priority pollutants and hazardous substances lists) should be provided.
- d. More in-depth procedures concerning metals analyses should be provided.
- e. Every effort should be made to obtain approval and funding for ongoing round robin QC checks among the various District, Division, and research laboratories.

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APPENDIX A: CORPS OF ENGINEERS WATER QUALITY LABORATORY POINTS OF CONTACT

District Laboratories

DISTRICT: New Orleans District Water Quality Laboratory

LABORATORY DIRECTOR: Merrick Blancq, (504) 733-5002

WATER QUALITY SUPERVISOR: Burnell Thibedeaux, (504) 838-2445

Mail Address: US Army Engineer District, New Orleans
PO Box 60267
New Orleans, LA 70160

DISTRICT: St. Louis District Water Quality Laboratory

LABORATORY DIRECTOR: Thomas J. Furdek, FTS 273-4008

WATER QUALITY SUPERVISOR: Theodore S. Postol, FTS 273-5031

Mail Address: US Army Engineer District, St. Louis
210 Tucker Blvd. N.
St. Louis, MO 63101

DISTRICT: Kansas City District

LABORATORY DIRECTOR: COL Gurnie Gunter, (816) 374-3201

WATER QUALITY SUPERVISOR: Robert L. Pearce, FTS 758-3773 (office)
FTS 758-2339 (laboratory)

Mail Address: US Army Engineer District, Kansas City
700 Federal Bldg.
Kansas City, MO 64106

Division Laboratories

DIVISION: Missouri River

LABORATORY DIRECTOR: R. K. Schlenker, FTS 864-3207

WATER QUALITY SUPERVISOR: Chris Dickey, FTS 864-3211

Mail Address: US Army Engineer Division, Missouri River
PO Box 103, Downtown Station
Omaha, NE 86101

DIVISION: New England Division

LABORATORY DIRECTOR: Michael J. Carroll, FTS 839-7392

WATER QUALITY SUPERVISOR: Robert X. Brazeau, (617) 894-2400 Ext. 392

Mail Address: US Army Engineer Division, New England
424 Trapelo Road
Waltham, MA 02254

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GUIDELINES FOR WATER QUALITY LABORATORY OPERATIONS(U)
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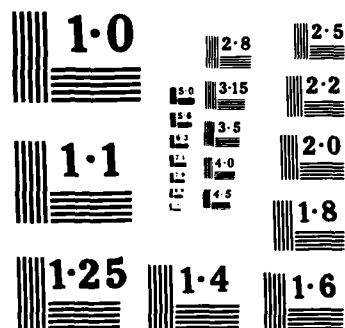
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NATIONAL BUREAU OF STANDARDS
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DIVISION: North Pacific Division Materials Laboratory
LABORATORY DIRECTOR: James Paxton, (503) 665-4166
WATER QUALITY SUPERVISOR: Joan Van den Akker, FTS 423-5566
Mail Address: US Army Engineer Division, North Pacific
North Pacific Division Materials Laboratory
Rt. 2. Box 12A
Troutdale, OR 97060

DIVISION: Ohio River Division Laboratory
LABORATORY DIRECTOR: David A. Lienhart, (513) 684-8694, FTS 684-8694
WATER QUALITY SUPERVISOR: Tayseer A. Gouda
Mail Address: Ohio River Division, Corps of Engineers
PO Box 27168, Madisonville Station
Cincinnati, OH 45227

DIVISION: South Atlantic Division (SAD Laboratory)
LABORATORY DIRECTOR: Robert J. Stephenson, (404) 429-5296
WATER QUALITY SUPERVISOR: James F. Nowland, (404) 429-5270
Mail Address: South Atlantic Division Laboratory
Corps of Engineers
611 South Cobb Drive (Ga. Hwy 280)
Marietta, GA 30061

DIVISION: South Pacific Division Laboratory
LABORATORY DIRECTOR: Thomas Chamberland, FTS 556-1245
WATER QUALITY SUPERVISOR: Ray V. Neuman, FTS 556-1245
Mail Address: South Pacific Division
PO Box 37
Sausalito, CA 94966

DIVISION: Southwestern Division Laboratory
LABORATORY DIRECTOR: Arthur H. Feese, (214) 767-2411
WATER QUALITY SUPERVISOR: Jeffrey Tye, (214) 767-2411
Mail Address: SWD Laboratory
4815 Cass Street
Dallas, TX 75235

Research Laboratories

RESEARCH FACILITY: U.S. Army Construction Engineering Research
Laboratory (CERL)

LABORATORY DIRECTOR: COL Louis J. Circeo

WATER QUALITY SUPERVISOR: Walt Mikucki/Dr. Ed Smith, FTS 958-7232
Dr. Ray Vogel, (217) 352-6511,
ext 430; (217) 333-7327

Mail Address: Construction Engineering Research Laboratory
Corps of Engineers
PO Box 4005
Champaign, IL 61820

FACILITY: Cold Regions Research and Engineering Laboratory (CRREL)

LABORATORY DIRECTOR: COL Wayne Hansen

WATER QUALITY SUPERVISOR: Thomas F. Jenkins, FTS 836-4385
Dan Legett, FTS 836-4393

Mail Address: Cold Regions Research and Engineering Laboratory
Corps of Engineers
Hanover, NH 03755

FACILITY: U.S. Army Engineer Waterways Experiment Station (WES)

LABORATORY DIRECTOR: COL Robert C. Lee

WATER QUALITY SUPERVISOR: Ann B. Strong, FTS 542-2726

Mail Address: US Army Engineer Waterways Experiment Station
PO Box 631
Vicksburg, MS 39180

APPENDIX B: US ENVIRONMENTAL PROTECTION AGENCY REGIONAL QUALITY ASSURANCE
COORDINATORS

REGION I

Wayne Wirtanen
Central Regional Laboratory
Environmental Services Division
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Lexington, MA 02173
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COML: 617-861-6700 Ext 205

REGION II

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Research and Quality Assurance
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REGION III

Charles Jones, Jr.
(3SA60)
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Philadelphia, PA 19106
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COML: (215) 597-9162

REGION IV

Wade Knight
Laboratory Services Branch
Environmental Services Division
College Station Road
Athens, GA 30613
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COML: (404) 546-3165

REGION V

David Payne
Quality Assurance Office
Environmental Services Division
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REGION VI

Robert Forrest
Environmental Services Division
1201 Elm St., First Int'l Bldg.
Dallas, TX 75270
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REGION VII

Charles P. Hensley
Laboratory Branch
Environmental Services Division
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Kansas City, KS 66115
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REGION VIII

Juanita Hillman
Environmental Services Division
Lincoln Tower Bldg., Suite 900
1860 Lincoln Street
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FTS: 327-4935
COML: (303) 837-4935

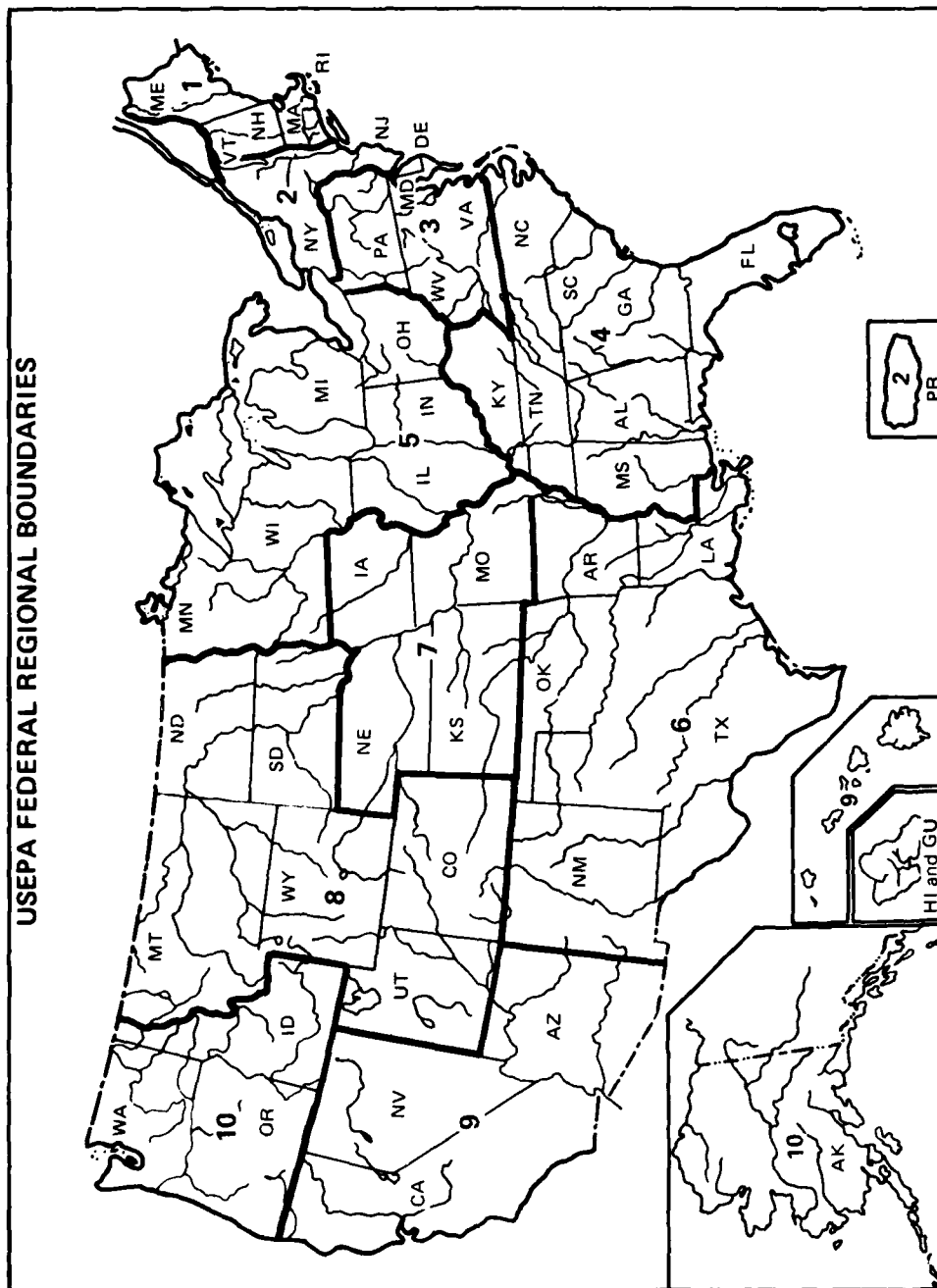
REGION IX

Ho Lee Young
Office of Quality Assurance and
Monitoring Systems
215 Fremont Street
San Francisco, CA 94105
FTS: 454-8002
COML: (415) 556-8002

REGION X

Barry Townes
Environmental Services Division
1200 Sixth Avenue
Seattle, WA 98101
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COML: (206) 442-1675

USEPA FEDERAL REGIONAL BOUNDARIES



APPENDIX C: US ENVIRONMENTAL PROTECTION AGENCY TECHNICAL INFORMATION
MANAGERS

OEPER - Office of
Environmental Processes
and Effects Research

Greg Grinder
USEPA, OEPER
RD-682
401 M St. S.W.
Washington, DC 20460

FTS: 382-5981
COML: (202) 382-5981

OEET - Office of
Environmental Engineer-
ing and Technology

Dave Graham
USEPA, OEET
RD-681
401 M St. S.W.
Washington, DC 20460

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COML: (202) 382-2600

OMSQA - Office of
Monitoring Systems and
Quality Assurance

Wanda Douglas
USEPA, OMSQA
RD-680
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Washington, DC 20460

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OHR - Office of Health
Research

Cliff Moore
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RD-683
401 M St. S.W.
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OHEA - Office of Health
and Environmental
Assessment

Marie Pfaff
USEPA, OHEA
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Washington, DC 20460

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OER - Office of
Exploratory Research

Don Cook
USEPA, OER
RD-675
401 M St. S.W.
Washington, DC 20460

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COML: (202) 382-5736

OEPER

ERL-Athens Environmental Research Laboratory-Athens	Bob Ryans USEPA, ERL College Station Rd. Athens, GA 30613	FTS: 250-3306 COML: (404) 546-3306
ESRL-RTP Environmental Sciences Research Laboratory- Research Triangle Park	Jim Upham USEPA, ESRL MD-59 Research Triangle Park, NC 27711	FTS: 629-2891 COML: (919) 541-2891
RSKERL-Ada Robert S. Kerr Environmental Research Laboratory-Ada	Marvin Wood USEPA, ERL P.O. Box 1198 Ada, OK 74820	FTS: 743-2226 COML: (405) 332-2226
ERL-Duluth Environmental Research Laboratory-Duluth	Carol Ann Curtis USEPA, ERL 6201 Congdon Blvd. Duluth, MN 55804	FTS: 783-9718 COML: (218) 727-9718
ERL-Corvallis Environmental Research Laboratory-Corvallis	Karen Randolph USEPA, ERL 200 S.W. 35th St. Corvallis, OR 97333	FTS: 420-4637 COML: (503) 757-4637
ERL-Narg. Environmental Research Laboratory-Narragansett	Stan Hegre USEPA, ERL Narragansett, RI 02882	FTS: 838-5087 Ext. 240 COML: (401) 789-1091 Ext. 240
ERL-Gulf Breeze Environmental Research Laboratory-Gulf Breeze	Betty Jackson USEPA, ERL Sabine Island Gulf Breeze, FL 32561	FTS: 686-9011 COML: (904) 932-9011

OEET

IERL-RTP Industrial Environmental Research Laboratory- Research Triangle Park	Bill Whelan USEPA, IERL MD-64 Research Triangle Park, NC 27711	FTS: 629-2216 COML: (919) 541-2216
IERL-Ci Industrial Environmental Research Laboratory- Cincinnati	Thelma Johnson USEPA, IERL Cincinnati, OH 45268	FTS: 684-7212 COML: (513) 684-7212
MERL-Ci Municipal Environmental Research Laboratory- Cincinnati	Marion Curry USEPA, MERL Cincinnati, OH 45268	FTS: 684-7748 COML: (513) 684-7748

OMSQA

EMSL-Ci Environmental Monitoring and Support Laboratory- Cincinnati	Margaret Owens USEPA, EMSL Cincinnati, OH 45268	FTS: 684-7301 COML: (513) 684-7301
EMSL-RTP Environmental Monitoring and Support Laboratory- Research Triangle Park	Seymour Hochheiser USEPA, EMSL MD-75 Research Triangle Park, NC 27711	FTS: 629-2106 COML: (919) 541-2106
EMSL-LV Environmental Monitoring and Support Laboratory- Las Vegas	Faye Cromar USEPA, EMSL P.O. Box 15027 Las Vegas, NV 89114	FTS: 545-2525 COML: (702) 798-2525

OHR

HERL-Ci Health Effects Research Laboratory-Cincinnati	Sandy Underwood USEPA, HERL Cincinnati, OH 45268	FTS: 684-7249 COML: (513) 684-7249
HERL-RTP Health Effects Research Laboratory-Research Triangle Park	Ferris Benson USEPA, HERL MD-70 Research Triangle Park, NC 27711	FTS: 629-2909 COML: (919) 541-2909

OHEA

ECAO-RTP Environmental Criteria and Assessment Office- Research Triangle Park	Vandy Bradow USEPA, ECAO MD-52 Research Triangle Park, NC 27711	FTS: 629-3797 COML: (919) 541-3797
ECAO-Ci Environmental Criteria and Assessment Office- Cincinnati	Dave Reisman USEPA, ECAO Cincinnati, OH 45268	FTS: 684-7573 COML: (513) 684-7573

APPENDIX D: U.S. GEOLOGICAL SURVEY INFORMATION SOURCES

HEADQUARTERS

U.S. Geological Survey
(Mail Stop Number) National Center
12201 Sunrise Valley Drive
Reston, VA 22092
Telephone (703) 860-extension
FTS 928-extension

Position	Official	Telephone Extension	Mail Stop
Chief Hydrologist.	Philip Cohen	6921	409
Associate Chief Hydrologist.	Russell H. Langford	6921	408
Program Officer.	Francis B. Sessums	6992	406A
Office of International Hydrology, Chief	Della Laura	6547	470
Office of Water Data Coordination, Chief.	Porter E. Ward	6931	417
National Water-Resources Conditions Program, Chief.	David W. Moody	6925	409
Assistant Chief Hydrologist for Operations	Thomas J. Buchanan	6801	441
Deputy Assistant Chief for Operations	Bruce K. Gilbert	6801	441
Finance and Fiscal Analysis Section, Chief	Clara L. Chambliss	6813	443
Operation Section, Chief	Alberto Condes	6861	405
Manpower Section, Chief.	Jerry C. Stephens	6944	406
Planning Section, Chief.	George E. Williams	6941	404
Instrumentation Group, Chief	Richard W. Paulson	6014	460
Assistant Chief Hydrologist for Research and Technical Coordination	Gordon D. Bennett	6971	414
Deputy Assistant Chief Hydrologist for Research and Technical Coordination	Roger G. Wolff	6971	413
Ground Water Branch, Chief	Eugene P. Patten, Jr.	6904	411
Quality of Water Branch, Chief.	R. J. Pickering	6834	412
Surface Water Branch, Chief.	Marshall E. Moss	6837	415
Office of Hazardous Waste Hydrology, Chief	John B. Robertson	6976	410
Coal and Oil-Shale Hydrology, Coordinator.	Solomon M. Lang	6846	407
Systems Analysis Group, Chief.	Robert M. Hirsh	6927	410
Assistant Chief Hydrologist for Scientific Publications and Data Management.	William B. Mann IV, Acting	6878	440
Deputy Assistant Chief Hydrologist for Scientific Publications and Data Management	John E. Moore	6878	440

<u>Position</u>	<u>Official</u>	<u>Telephone Extension</u>	<u>Mail Stop</u>
Office of Scientific Information, Chief.	John E. Moore	6878	440
National Water-Use Information Program, Manager	William B. Mann IV	6878	440
Scientific Publications Program, Chief.	Eugene R. Hampton	6881	439
Office of Computer Technology, Chief.	J. Ronald Jones	6877	440
National Water-Data Storage and Retrieval System, Chief.	Charles R. Showen	6871	437
Branch of Water Information Transfer, Manager.	Gary D. Cobb	6031	421
National Water Data Exchange, Manager.	Melvin D. Edwards	6031	421
Water Resources Scientific Information Center, Manager.	Raymond A. Jensen	7455	423
Environmental Affairs Program, Chief (Acting)	Richard A. Watkins	7455	423
Information Transfer Program, Manager.	Kenneth H. Suter	6867	421

REGIONAL HYDROLOGISTS

Northeastern Region

Connecticut, Delaware, Illinois, Indiana, Maine, Maryland, Massachusetts, Michigan, Minnesota, New Hampshire, New Jersey, New York, Ohio, Pennsylvania, Rhode Island, Vermont, Virginia, Washington, D.C., West Virginia, Wisconsin

Office of the Regional Hydrologist

Address:

Regional Hydrologist
U.S. Geological Survey
National Center, Mail Stop 433
12201 Sunrise Valley Drive
Reston, VA 22092
Telephone: (703) 860-6985; FTS 928-6985
Office hours: 7:45 a.m. to 4:15 p.m. Eastern Time

Southeastern Region

Alabama, Arkansas, Florida, Georgia, Kentucky, Louisiana, Mississippi, North Carolina, Puerto Rico, South Carolina, Tennessee, Virgin Islands

Office of the Regional Hydrologist

Address:

Regional Hydrologist
U.S. Geological Survey
Richard B. Russell Federal Bldg.
75 Spring Street, SW, Rm. 772
Atlanta, GA 30303
Telephone: (404) 221-5174; FTS 242-5174
Office hours: 7:30 a.m. to 4:15 p.m. Eastern Time

Central Region

Colorado, Iowa, Kansas, Missouri, Montana, Nebraska, New Mexico, North Dakota, Oklahoma, South Dakota, Texas, Utah, Wyoming

Office of the Regional Hydrologist

Mailing address:

Regional Hydrologist
U.S. Geological Survey
Mail Stop 406, Box 25046
Denver Federal Center
Lakewood, CO 80225

Office address:

Denver Federal Center, Bldg. 25
Lakewood, CO 80225
Telephone: (303) 234-3661; FTS 234-3661
Office hours: 8:00 a.m. to 4:30 p.m. Mountain Time

Western Region

Alaska, Arizona, California, Guam, Hawaii, Idaho, Nevada, Oregon, Washington

Office of the Regional Hydrologist

Address:

Regional Hydrologist
U.S. Geological Survey
345 Middlefield Road, Mail Stop 66
Menlo Park, CA 94025
Telephone: (415) 323-8111, ext. 2337; FTS 467-2337
Office hours: 7:45 a.m. to 4:15 p.m. Pacific Time

REGIONAL RESEARCH HYDROLOGISTS

Office of the Assistant Chief Hydrologist for
Research and Technical Coordination

Deputy Assistant Chief Hydrologist for
Research and Technical Coordination

Address:

U.S. Geological Survey
413 National Center
2201 Sunrise Valley Drive
Reston, VA 22092
Telephone: (703) 860-6971; FTS 928-6971
Office hours: 7:45 a.m. to 4:15 p.m. Eastern Time

Offices of the Regional Research Hydrologists

Northeastern Region

Address:

Regional Research Hydrologist, NR
U.S. Geological Survey
432 National Center
12201 Sunrise Valley Drive
Reston, VA 22092
Telephone: (703) 860-6958; FTS 928-6958
Office hours: 7:45 a.m. to 4:15 p.m. Eastern Time

Southeastern Region

Address:

Regional Research Hydrologist, SR
U.S. Geological Survey
Gulf Coast Hydrosience Center
Building 1100, Room 312
NSTL Station, MS 39529
Telephone: (601) 688-3130; FTS 494-1512
Office hours: 8:00 a.m. to 4:30 p.m. Central Time

Central Region

Address:

Regional Research Hydrologist, CR
U.S. Geological Survey
Mail Stop 412, Box 25046
Denver Federal Center, Bldg. 25
Lakewood, CO 80225
Telephone: (303) 234-4175; FTS 234-4175
Office hours: 8:00 a.m. to 4:30 p.m. Mountain Time

Western Region

Address:

Regional Research Hydrologist, WR
U.S. Geological Survey
Mail Stop 66
345 Middlefield Road
Menlo Park, CA 94025
Telephone: (415) 323-8111, ext. 2339; FTS 467-2339
Office hours: 7:45 a.m. to 4:15 p.m. Pacific Time

APPENDIX E: PART III PUBLICATIONS AND HELPFUL REFERENCES CONCERNING
WATER QUALITY LABORATORY OPERATIONS

Basic References

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Laboratory quality
assurance/quality control

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APPENDIX F: APPROVED TEST PROCEDURES AND PROPOSED CHANGES TO THE
"GUIDELINES ESTABLISHING TEST PROCEDURES FOR THE
ANALYSIS OF POLLUTANTS UNDER THE CLEAN WATER ACT"
(From: Federal Register, Vol 49, No. 209, Friday,
October 26, 1984).

TABLE F1.—LIST OF APPROVED BIOLOGICAL TEST PROCEDURES

Parameter and units	Method ¹	EPA ²	Reference (Method Number or Page)		
			Standard Methods 15th Ed.	ASTM	USGS
Bacteria.					
1 Coliform (fecal) number per 100 ml	MPN, 5 tube, 3 dilution; or, membrane filter (MF) ³ , single step.....	p. 132..... p. 124.....	960C..... 909C.....		B-0050-77
2 Coliform (fecal) in presence of chlorine number per 100 ml.....	MPN, 5 tube, 3 dilution.....	p. 132.....	908C.....		
3 Coliform (total) number per 100 ml.....	MPN, 5 tube, 3 dilution; or, MF ³ single step or two step.....	p. 114..... p. 108.....	908A..... 909A.....		B-0025-77
4 Coliform (total) in presence of chlorine, number per 100 ml.....	MPN, 5 tube, dilution; or MF ³ with enrichment.....	p. 114..... p. 111.....	908A..... 909 (A + A.5c).....		
5 Fecal streptococci, number per 100 ml.....	MPN, 5 tube, 3 dilution; MF ³ ; or, plate count.....	p. 139..... p. 136..... p. 143.....	910A..... 910B..... 910C.....		B0055-77. ⁴

¹ The method must be specified when results are reported.² "Microbiological Methods for Monitoring the Environment, Water and Wastes, 1978", EPA-600/6-78-017, U.S. Environmental Protection Agency.³ Greeson, P. E., et al. Methods for Collection and Analysis of Aquatic Biological and Microbiological Samples, "U.S. Geological Survey, Techniques of Water-Resources Investigations, Book 5, Chapter A4, Laboratory Analysis, 1977.⁴ 0.45 um membrane filter or other pore size certified by the manufacturer to fully retain organisms to be cultivated, and free of extractables which could interfere with their growth and development.⁵ Approved only if dissolution of the KF Streptococcus Agar (Section 5.1, USGS Method B-0055-77) is made in a boiling water bath to avoid scorching of the medium.

TABLE F2.—LIST OF APPROVED INORGANIC TEST PROCEDURES

Parameter, units, and method	Reference (method No. or page)				
	EPA 1979	Standard methods 15th Ed.	ASTM	USGS ¹	Other
1. Acidity, as CaCO ₃ , mg/L: Electrometric end point or phenolphthalein end point.	305.1.....	402(4.d).....	D1067-70(E).....		
2. Alkalinity, as CaCO ₃ , mg/L: Electrometric or colorimetric:					
Titration to pH 4.5, manual	310.1.....	403.....	D1067(B).....	I-1030-78.....	P 548 ^a
Or automated	310.2.....			I-2030-78.....	
3. Aluminum—Total ^a , mg/L: Digestion ^a followed by:					
AA direct aspiration	202.1.....	303C.....		I-3051-78.....	
AA furnace	202.2.....	304.....			Method 200.7 ^a
Inductively coupled plasma					
Or colorimetric (Eriochrome cyanine R)		306B.....			
4. Ammonia (as N), mg/L: Manual distillation ^a (at pH 8.5):					
Followed by:	350.2.....	417A.....			
Nesslerization	350.2.....	417B.....	D1426-79(A).....	I-3520-78.....	P 553 ^a
Titration	350.2.....	417D.....			
Electrode	350.3.....		D1426-79(J).....		
Automated phenate, or	350.1.....	417F.....	D1426-79(L).....	I-4523-78.....	
Automated electrode					^a
5. Antimony—Total ^a , mg/L: Digestion ^a followed by:					
AA direct aspiration	204.1.....	303A.....			
AA furnace, or	204.2.....	304.....			Method 200.7 ^a
Inductively coupled plasma					
6. Arsenic—Total ^a , mg/L:					
Digestion ^a followed by:	206.5.....				
Hydride	206.3.....	303E.....	D2972-78(B).....	I-3062-78.....	
AA furnace	206.2.....	304.....			Method 200.7 ^a
Inductively coupled plasma					
Or, colorimetric (SDDC)	206.4.....	307B.....	D2972-78(A).....	I-3060-78.....	
7. Barium—Total ^a , mg/L: Digestion ^a followed by:					
AA direct aspiration	208.1.....	303C.....		I-3064-78.....	
AA furnace, or	208.2.....	304.....			Method 200.7 ^a
Inductively coupled plasma					
8. Beryllium—Total ^a , mg/L: Digestion ^a followed by:					
AA direct aspiration	210.1.....	303C.....	D3845-78.....	I-3095-78.....	
AA furnace	210.2.....	304.....			

TABLE F2.—LIST OF APPROVED INORGANIC TEST PROCEDURES—Continued

Parameter, units, and method	Reference (method No. or page)				
	EPA 1978	Standard methods 15th Ed.	ASTM	USGS ¹	Other
Inductively coupled plasma Or colorimetric (aluminum)		309B			Method 200.7 ^a
9 Biochemical oxygen demand (BOD ₅), mg/L Winkler (Azide modification) Or electrode method	405.1	507		I-1578-78	P. 17 ^a P. 548 ^a
10 Bismuth—Total, mg/L Colorimetric (curcumin) or Inductively coupled plasma	212.3	404A		I-3112-78	Method 200.7 ^a P. 544 ^a
11 Bromide, mg/L Titrimetric	320.1		D1246-77(C)	I-1125-78	
12 Cadmium—Total ² , mg/L Digestion ² followed by AA direct aspiration AA furnace	213.2 213.2	303A or 303B 304	D3557-78 (A or B)	I-3135-78 or I-3136-78	P ₂ 557 ^a P. 37 ^a
Inductively coupled plasma volumetric ² or Colorimetric (Dithione)		310B	D3557-78(C)		Method 200.7 ^a
13 Calcium—Total ² , mg/L Digestion ² followed by Atomic absorption Inductively coupled plasma Or EDTA titration	215.1 215.2	302A 311C 507(S e 6)	D511-77(C) D511-77(B)	I3152-78	Method 200.7 ^a
14 Carbonaceous Biochemical oxygen demand (CBOD ₅), mg/L Winkler (Azide modification) or electrode method with nitrification inhibitor					
15 Chemical oxygen demand (COD), mg/L Titrimetric colorimetric Manual or Automated Spectrophotometric	410.1 410.2 410.3 410.4	508A	D1252-78	I-3580-78 I-3582-78 I-3581-78	P. 550 ^a and P. 17 ^a and (1 ^a)
16 Chloride, mg/L Titrimetric (silver nitrate) or Mercuric nitrate Colorimetric (mercuric cyanide) manual or Automated	325.3 325.1 or 325.2	407A 407B 407D	D512-57(B) D512-67(A) D512-67(C)	I-1183-78 I-1184-78 I-1187-78 I-2187-78	P. 554 ^a
17 Chlorine—Total residual, mg/L Titrimetric amperometric ¹¹ Starch end point Iodometric or DPO FAS Spectrophotometric, DPD, or Electrode	330.1 330.2 330.3 330.4 330.5	408C 408B 408A 408D 408E	D1253-78(A)		(1 ^a)
18 Chromium VI dissolved, mg/L 0.45 micron Nitration with Extraction and atomic absorption, or Colorimetric (Diphenylcarbazide)	218.4	303B		I-1212-78 I-1230-78	
9 Chromium—Total ² , mg/L Digestion ² (optional extraction) followed by AA direct aspiration AA furnace Inductively coupled plasma Or colorimetric (Diphenylcarbazide)	218.3 218.1 218.2	303A or 303B 304	D1607-77(D)	I-3236-78	P. 557 ^a Method 200.7 ^a
20 Cobalt—Total ² , mg/L Digestion ² followed by AA direct aspiration AA furnace or Inductively coupled plasma	219.1 219.2	303A or 303B 304	D3558-77 (A or B)	I-3240-78 or I-3239-78	P. 37 ^a
21 Color, platinum Cobalt units or dominant wavelength hue luminance purity Colorimetric, ADIM Platinum cobalt, or Spectrophotometric	110.1 110.2 110.3	204D 204A 204B		I-1250-78	(1 ^a)
22 Copper—Total ² , mg/L Digestion ² followed by AA direct aspiration AA furnace Inductively coupled plasma Colorimetric (neocuproine) Bismuthimetric	220.1 220.2	303A or 303B 304	D1668-77 (D or E)	I-3271-78 or I-3270-78	P. 557 ^a and P. 37 ^a Method 200.7 ^a
23 Cyanide, mg/L Manual distillation with HCN ₂ Followed by titrimetric Manual or Automated ¹¹ spectrophotometric	335.2 335.2 335.2 335.3	412D 412B 412C 412D	D2036-75(A) D2036-75(A) D2036-75(B)	I-3300-78	P. 22 ^a
24 Cyanide amenable to oxidation, mg/L Manual distillation with HCN ₂ Followed by titrimetric manual or automated ¹¹ spectrophotometric	335.1	412F			
25 Fluoride—Total, mg/L Manual distillation ¹ Followed by manual or Automated electrode SPADNS Or automated complexone	340.2 340.1 340.3	413A 413B 413C 413E	D1179-72(B) D1179-72(A)	I-4127-78	
26 Gold—Total ² , mg/L Digestion ² followed by AA direct aspiration Or AA furnace	231.1 231.2	303A 304			
27 Hardness—Total as CaCO ₃ , mg/L Automated colorimetric EDTA titration Inductively coupled plasma Or atomic absorption (sum of Ca and Mg as their respective carbonates)	130.1 130.2 215.1 + 242.1	314B 303A	D1125-67(3)	I-1338-78 I-3153-78 + I-3448-78	Method 200.7 ^a

TABLE F2.—LIST OF APPROVED INORGANIC TEST PROCEDURES—Continued

Parameter, units, and method	Reference (method No. or page)				
	EPA 1979	Standard methods 15th Ed.	ASTM	USGS ¹	Other
26. Hydrogen ion (pH), pH units: Electrometric	150.1	423	D1283-78(A) or D1283-78(B)	I-1588-78	(=)
Measurements: or automated electrode					
28. Indium—Total ² , mg/L: Digestion ³ followed by: AA direct aspiration	235.1	303A			
Or AA furnace	235.2	304			
30. Iron—Total ² , mg/L: Digestion ³ followed by: AA direct aspiration	236.1	303A or 303B	D1068-77 (C or D)	I-3381-78	P. 557. ²
AA furnace	236.2	304			
Inductively coupled plasma					Method 200.7. ⁴
Or colorimetric (Phenanthroline)		315B	D1068-77(A)		(¹¹)
31. Kjeldahl nitrogen—Total (as N), mg/L: Digestion and distillation	351.3	420A or B			P. 552. ²
Followed by titration	381.3	417D	D3590-77		
Nesslerization or	351.3	417B			
Electrode	351.3	417E		I-4551-78	
Automated phenate	351.1			I-4552-78	
Semi-automated block digester	351.2				
Or potentiometric	351.4				
32. Lead—Total ² , mg/L: Digestion ³ followed by: AA direct aspiration	239.1	303A or 303B	D3559-78 (A or B)	I-3399-78	P. 557. ²
AA furnace	239.2	304			
Inductively coupled plasma					Method 200.7. ⁴
Voltammetry ⁵ or			D3559-78(C)		
Colorimetric (Dithione)		316B			
33. Magnesium—Total ² , mg/L: Digestion ³ followed by: Atomic absorption	242.1	303A	D511-77(B)	I-3447-78	P. 557. ²
Inductively coupled plasma					Method 200.7. ⁴
Or gravimetric		318B	D511-77(A)		
34. Manganese—Total ² , mg/L: Digestion ³ followed by: AA direct aspiration	243.1	303A or 303B	D858-77 (B or C)	I-3454-78	P. 557. ²
AA furnace	243.2	304			
Inductively coupled plasma					Method 200.7. ⁴
Or colorimetric (Persulfate)		319B	D858-77(A)		P. 564. ²
Periodate					18.
35. Mercury—Total ² , mg/L: Cold vapor, manual or	245.1	303F	D3223-79	I-3482-78	P. 558. ²
Automated	245.2				
36. Molybdenum—Total ² , mg/L: Digestion ³ followed by: AA direct aspiration	246.1	303C		I-3490-78	
AA furnace, or	246.2	304			
Inductively coupled plasma					Method 200.7. ⁴
37. Nickel—Total ² , mg/L: Digestion ³ followed by: AA direct aspiration	249.1	303A or 303B	D1886-77 (C or D)	I-3499-78	
AA furnace	249.2	304			
Inductively coupled plasma					Method 200.7. ⁴
Or colorimetric (Heptoxime)		321B			
38. Nitrate (as N), mg/L: Bromine sulfate, or	352.1		D092-71		P. 554. ²
Nitrate-nitrite N minus Nitrite N	See parameters 39 and 40.	See parameters 39 and 40.	See parameters 39 and 40.	See parameters 39 and 40.	P. 28. ²
39. Nitrate-nitrite (as N), mg/L: Cadmium reduction, manual	353.3	418C	D3867-79(B)		
Or automated, or	353.2	418F	D3867-79(A)	I-4545-78	
Automated hydrazine	353.1				
40. Nitrite (as N), mg/L: Spectrophotometric, manual or	354.1	419	D1254-87		19.
Automated (Diazotization)				I-4540-78	
41. Oil and grease—Total recoverable, mg/L: Gravimetric (extraction)	413.1	503A			
42. Organic carbon—Total (TOC), mg/L: Combustion or oxidation	415.1	505	D2579-78(A) or D2579-78(B)		P. 551. ² and P. 4. ²²
43. Organic nitrogen (as N), mg/L: Total Kjeldahl N minus ammonia N	See parameters 31 and 4	420A	D3590-77 minus D1426-79(A)	See parameters 31 and 4	PP. 552-53. ²
44. Orthophosphate (as P), mg/L: Ascorbic acid method, automated	365.1	424G		I-4601-78	P. 561. ²
Or manual single reagent or	365.2	424F	D515-78(A)		
Manual two reagent	365.3				
45. Osmium—Total ² , mg/L: Digestion ³ followed by: AA direct aspiration, or	252.1	303C			
AA furnace	252.2	304			
46. Oxygen, dissolved, mg/L: Winkler (Azide modification)	360.2	421B	D1589-80(A)	I-1575-78	P. 550. ²
Or electrode	360.1	421F		I-1576-78	
47. Palladium—Total ² , mg/L: Digestion ³ followed by: AA direct aspiration	253.1				P. 527. ²²
Or AA furnace	253.2				P. 528. ²²
48. Phenols, mg/L: Manual distillation	420.1		D1783-70 (A or B)		26.
Followed by manual	420.1				26.
Or automated ¹⁶ colorimetric (4AAP)	420.2				
49. Phosphorus (elemental), mg/L: Gas-liquid chromatography					21.

TABLE F2.—LIST OF APPROVED INORGANIC TEST PROCEDURES—Continued

Parameter, units, and method	Reference (method No. or page)				
	EPA 1970	Standard methods 15th Ed.	ASTM	USGS ¹	Other
50 Phosphorus—Total, mg/L: Persulfate digestion Followed by manual or Automated ascorbic acid Reduction, or semi-automated block digester	365.2 365.2 or 365.3 365.1 365.4	424C (III) 424F 424G	D515-78(A)	I-4800-78 I-4803-78	P. 561. ^a
51 Platinum—Total ^a , mg/L. Digestion ^a followed by: AA direct aspiration Or AA furnace	255.1 255.2	303A 304			
52 Potassium—Total ^a , mg/L. Digestion ^a followed by: Atomic absorption Inductively coupled plasma Or flame photometric	256.1	303A 322B 209A	D1428-84(A)	I-3630-78	P. 560. ^a Method 200.7. ^a
53 Residue—total, mg/L. Gravimetric, 103-105°C	180.3	209B		I-3750-78	
54 Residue—filterable, mg/L. Gravimetric, 180°C	180.1	209B		I-1750-78	
55 Residue—nonfilterable, (TSS), mg/L. Gravimetric, 103-105°C post washing of residue	180.2	209D		I-3765-78	
56 Residue—settlesable, mg/L. Volumetric (Imhoff cone) or gravimetric	180.5	209F			
57 Residue—volatile, mg/L. Gravimetric, 550°C	180.4	209E		I-3753-78	
58 Rhodium—Total ^a , mg/L. Digestion ^a followed by: AA direct aspiration Or AA furnace	265.1 267.2	303A 304			
59 Ruthenium—Total ^a , mg/L. Digestion ^a followed by: AA direct aspiration Or AA furnace	267.1 267.2	303A 304			
60 Selenium—Total ^a mg/L. Digestion ^a followed by: AA furnace Inductively coupled plasma Or hydride	270.2 270.3	304 303E	D3659-79	I-3667-78	Method 200.7. ^a
61 Silica—Dissolved, mg/L. 0.45 micron filtration: Followed by manual or Automated colorimetric (Molybdoascorbate), or Inductively coupled plasma	370.1	425C	D659-86(B)	I-1700-78 I-2700-78	Method 200.7. ^a
62 Silver—Total ^a mg/L. Digestion ^a followed by: AA direct aspiration AA furnace, or Inductively coupled plasma	272.1 272.1	303A or 303B 304		I-3720-78	P. 557. ^a and p. 37. ^a Method 200.7. ^a
63 Sodium—Total ^a , mg/L. Digestion ^a followed by: Atomic absorption Inductively coupled plasma Or flame photometric	273.1	303A		I-3735-78	P. 561. ^a Method 200.7. ^a
64 Specific conductance, mhos/cm. Wheatstone bridge	120.1	205	D1428-84(A) D1125-77(A)	I-1780-78	P. 547. ^a
65 Sulfate (as SO ₄), mg/L: Automated methylthymol blue Gravimetric, or Turbidimetric	375.2 375.3 375.4	426A or 426B 426C	D516-86(A) D516-86(B)	I-2622-78	PP. 562-63. ^a
66 Sulfide (as S), mg/L: Titrimetric (iodine) or Colorimetric (methylene blue)	376.1 376.2	427D 427C		I-3640-78	
67 Sulfite (as SO ₃), mg/L. Titrimetric (iodine iodate)	377.1	426F	D1339-78(C)		
68 Surfactants, mg/L. Colorimetric (methylene blue)	425.1	512A	D2330-68(A)		
69 Temperature, °C. Thermometric	170.1	212			(^a).
70 Thallium—Total ^a mg/L. Digestion ^a followed by: AA direct aspiration AA furnace, or Inductively coupled plasma	279.1 279.2	303A 304			Method 200.7. ^a
71 Tin—Total ^a mg/L. Digestion ^a followed by: AA direct aspiration or AA furnace	282.1 282.2	303A 304		I-3850-78	
72 Titanium—Total ^a mg/L. Digestion ^a followed by: AA direct aspiration or AA furnace	283.1 283.2	303C 304			
73 Turbidity, NTU. Nephelometric	180.1	214A	D1889-71	I-3860-78	
74 Vanadium—Total ^a mg/L. Digestion ^a followed by: AA direct aspiration AA furnace Inductively coupled plasma Or colorimetric (Gallate acid)	286.1 286.2	303C 304	D3373-75		Method 200.7. ^a
75 Zinc—Total ^a mg/L. Digestion ^a followed by: AA direct aspiration AA furnace Inductively coupled plasma Or colorimetric (Zincon)	289.1 289.2	303A or 303B 304	D1691-77(D) D1691-77(C)	I-3900-78	P. 557. ^a P. 37. ^a Method 200.7. ^a ^a .

TABLE F2.—LIST OF APPROVED INORGANIC TEST PROCEDURES—Continued

- ¹ "Methods for Analysis of Inorganic Substances in Water and Fluvial Sediments," U.S. Department of the Interior, U.S. Geological Survey, Open-File Report 78-679, or "Methods for Determination of Inorganic Substances in Water and Fluvial Sediments," N.W. Skougstad, et al, U.S. Geological Survey, Techniques of Water-Resources Investigations, Book 5, Chapter A1, 1979.
- ² "Official Methods of Analysis of the Association of Official Analytical Chemists," methods manual, 13th ed. (1980).
- ³ For the determination of total metals the sample is not filtered before processing. A digestion procedure is required to solubilize suspended material and to destroy possible organic-metal complexes. Two digestion procedures are given in "Methods for Chemical Analysis of Water and Wastes, 1979." One (§ 4.1.3), is a vigorous digestion using nitric acid. A less vigorous digestion using nitric and hydrochloric acids (§ 4.1.4) is preferred; however, the analyst should be cautioned that this mild digestion may not suffice for all sample types. Particularly, if a colorimetric procedure is to be employed, it is necessary to ensure that all organo-metallic bonds be broken so that the metal is in a reactive state. In those situations, the vigorous digestion is to be preferred making certain that at no time does the sample go to dryness. Samples containing large amounts of organic materials would also benefit by this vigorous digestion. Use of the graphite furnace technique, inductively coupled plasma, as well as determinations for certain elements such as arsenic, the noble metals, mercury, selenium, and titanium require a modified digestion and in all cases the method write-up should be consulted for specific instructions and/or cautions.
- ⁴ Note: If the digestion procedure for direct aspiration or graphite furnace atomic absorption analysis included in one of the other approved references is different than the above, the EPA procedure must be used.
- ⁵ Dissolved metals are defined as those constituents which will pass through a 0.45 micron membrane filter. Following filtration of the sample, the referenced procedure for total metals must be followed. Sample digestion of the filtrate for dissolved metals, or digestion of the original sample solution for total metals may be omitted for AA (direct aspiration or graphite furnace) and ICP analyses provided the sample has a low COD and the filtrate meets the following criteria:
- (a) is visibly transparent
 - (b) has no perceptible odor, and
 - (c) is free of particulate or suspended matter following acidification.
- ⁶ The full text of Method 200.7, "Inductively Coupled Plasma Atomic Emission Spectrometric Method for Trace Element Analysis of Water and Wastes," is given at Appendix C of this Part 136.
- ⁷ Manual distillation is not required if comparability data on representative effluent samples are on company file to show that this preliminary distillation step is not necessary; however, manual distillation will be required to resolve any controversies.
- ⁸ Ammonia, Automated Electrode Method, Industrial Method Number 379-75WE, dated February 19, 1976, Technicon AutoAnalyzer II, Technicon Industrial Systems, Tarrytown, New York 10591.
- ⁹ Carbonaceous biochemical oxygen demand (CBOD₅) must not be confused with the traditional BOD₅ test which measures "total BOD". The addition of the nitrification inhibitor is not a procedural option, but must be included to report the CBOD₅ parameter. A discharger whose permit requires reporting the traditional BOD₅ may not use a nitrification inhibitor in the procedure for reporting the results. Only when a discharger's permit specifically states CBOD₅ is required can the permittee report data obtained using the nitrification inhibitor.
- ¹⁰ American National Standard on Photographic Processing Effluents, Apr. 2, 1975. Available from ANSI, 1430 Broadway, New York, NY 10018.
- ¹¹ The use of normal and differential pulse voltage ramps to increase sensitivity and resolution is acceptable.
- ¹² Chemical Oxygen Demand, Method 8000, Hach Handbook of Water Analysis, 1979, Hach Chemical Company, P.O. Box 369, Loveland, Colorado 80537.
- ¹³ COD Method, Oceanography International Corporation, 512 West Loop, P.O. Box 2980, College Station, Texas 77840.
- ¹⁴ The back titration method will be used to resolve controversy.
- ¹⁵ National Council of the Paper Industry for Air and Stream Improvement, Inc., Technical Bulletin 253, December 1971.
- ¹⁶ Copper, Bismuthomate Method, Method 8506, Hach Handbook of Water Analysis, 1979, Hach Chemical Company, P.O. Box 369, Loveland, Colorado 80537.
- ¹⁷ After the manual distillation is completed, the auto-analyzer manifolds in EPA Methods 335.03 (Cyanide) or 420.2 (phenols) are simplified by connecting the re-sample line directly to the sampler. When using the manifold setup shown in Method 335, the buffer 6.2 should be replaced with the buffer 7.6 found in Method 335.2.
- ¹⁸ Hydrogen Ion (pH) Automated Electrode Method, Industrial Method Number 378-75WA, October 1976, Technicon Auto-Analyzer II, Technicon Industrial Systems, Tarrytown, New York 10591.
- ¹⁹ Iron, 1,10-Phenanthroline Method, Method 8008, 1980, Hach Chemical Company, P.O. Box 369, Loveland, Colorado 80537.
- ²⁰ Manganese, Periodate Oxidation Method, Method 8034, Hach Handbook of Wastewater Analysis, 1979, pages 2-113 and 2-117, Hach Chemical Company, Loveland, Colorado 80537.
- ²¹ Nitrogen, Nitrite, Method 8507, Hach Chemical Company, P.O. Box 369, Loveland, Colorado 80537.
- ²² Goerlitz, D., Brown, E., "Methods for Analysis of Organic Substances in Water," U.S. Geological Survey, Techniques of Water-Resources Investigations, Book 5, Chapter A3, p.4 (1972).
- ²³ R.F. Addison and R.G. Ackman, "Direct Determination of Elemental Phosphorus by Gas-Liquid Chromatography," Journal of Chromatography, Vol. 47, No. 3, pp. 421-426, 1970.
- ²⁴ Recommended methods for the analysis of silver in industrial wastewaters at concentrations of 1 mg/L and above are inadequate where silver exists as an inorganic halide. Silver halides such as the bromide and chloride are relatively insoluble in reagents such as nitric acid but are readily soluble in an aqueous buffer of sodium thiosulfate and sodium hydroxide to a pH of 12. Therefore, for levels of silver above 1 mg/L, 20 mL of sample should be diluted to 100 mL by adding 40 mL each of 2 M Na₂S₂O₃ and 2M NaOH. Standards should be prepared in the same manner. For levels of silver below 1 mg/L the recommended method is satisfactory.
- ²⁵ Stevens, H.H., Ficke, J.F., and Smoot, G.F., "Water Temperature-Influential Factors, Field Measurement and Data Presentation," U.S. Geological Survey, Techniques of Water-Resources Investigations, Book 1, Chapter D1, 1975.
- ²⁶ Zinc, Zincon Method, Method 8009, Hach Handbook of Water Analysis, 1979, pages 2-231 and 2-333, Hach Chemical Company, Loveland, Colorado 80537.
- ²⁷ "Selected Analytical Methods Approved and Cited by the United States Environmental Protection Agency," Supplement to the Fifteenth Edition of Standard Methods for the Examination of Water and Wastewater (1981).
- ²⁸ The approved method is that cited in Standard Methods for the Examination of Water and Wastewater, 14th Edition. The colorimetric reaction is conducted at a pH of 10.0 ± 0.2. The approved methods are given on pp. 576-81 of the 14th Edition: Method 510A for distillation, Method 510B for the manual colorimetric procedure, or Method 510C for the manual spectrophotometric procedure.
- ²⁹ ORION Research Instruction Manual, Residual Chlorine Electrode Model 97-70, 1977, Orion Research Incorporated, 640 Memorial Drive, Cambridge, Massachusetts 02138.

TABLE F3.—LIST OF APPROVED TEST PROCEDURES FOR NON-PESTICIDE ORGANIC COMPOUNDS

Parameter	EPA Method Number ^a			Other
	GC	GC/MS	HPLC	
1. Acenaphthene.....	610	625, 1625	610	
2. Acenaphthylene.....	610	625, 1625	610	
3. Acrolein.....	603	*624, 1624		
4. Acrylonitrile.....	603	*624, 1624		
5. Anthracene.....	610	625, 1625	610	
6. Benzene.....	602	624, 1624		
7. Benzidine.....		*625, 1625	605	Note 3, p. 1;
8. Benzo(a)anthracene.....	610	625, 1625	610	
9. Benzo(a)pyrene.....	610	625, 1625	610	
10. Benzo(b)fluoranthene.....	610	625, 1625	610	
11. Benzo(g,h,i)perylene.....	610	625, 1625	610	
12. Benzo(k)fluoranthene.....	610	625, 1625	610	
13. Benzyl Chloride.....				Note 3, p. 130; Note 6, p. 8102.
14. Benzyl Butyl Phthalate.....	606	625, 1625		
15. Bis(2-chloroethoxy) methane.....	611	625, 1625		
16. Bis(2-chloroethyl) ether.....	611	625, 1625		
17. Bis(2-ethylhexyl) phthalate.....	606	625, 1625		
18. Bromochloromethane.....	601	624, 1624		
19. Bromoform.....	601	624, 1624		
20. Bromomethane.....	601	624, 1624		
21. 4-Bromophenylphenyl ether.....	611	625, 1625		
22. Carbon tetrachloride.....	601	624, 1624		Note 3, p. 130;
23. 4-Chloro-3-methylphenol.....	604	625, 1625		
24. Chlorobenzene.....	601, 602	624, 1624		Note 3, p. 130;
25. Chloroethane.....	601	624, 1624		
26. 2-Chloroethylvinyl ether.....	601	624, 1624		
27. Chloroform.....	601	624, 1624		Note 3, p. 130;
28. Chloromethane.....	601	624, 1624		
29. 2-Chloronaphthalene.....	612	625, 1625		
30. 2-Chlorophenol.....	604	625, 1625		
31. 4-Chlorophenylphenyl ether.....	611	625, 1625		
32. Chrysene.....	610	625, 1625	610	
33. Dibenzo(a,h)anthracene.....	610	625, 1625	610	
34. Dibromochloromethane.....	601	624, 1624		
35. 1,2-Dichlorobenzene.....	601, 602, 612	624, 625, 1625		
36. 1,3-Dichlorobenzene.....	601, 602, 612	624, 625, 1625		
37. 1,4-Dichlorobenzene.....	601, 602, 612	625, 1624, 1625		
38. 3,3'-Dichlorobenzidine.....		625, 1625	605	
39. Dichlorodifluoromethane.....	601			
40. 1,1-Dichloroethane.....	601	624, 1624		
41. 1,2-Dichloroethane.....	601	624, 1624		
42. 1,1-Dichloroethene.....	601	624, 1624		
43. trans-1,2-Dichloroethene.....	601	624, 1624		
44. 2,4-Dichlorophenol.....	604	625, 1625		
45. 1,2-Dichloropropene.....	601	624, 1624		
46. cis-1,3-Dichloropropene.....	601	624, 1624		
47. trans-1,3-Dichloropropene.....	601	624, 1624		
48. Diethyl phthalate.....	606	625, 1625		

TABLE F3—LIST OF APPROVED TEST PROCEDURES FOR NON-PESTICIDE ORGANIC COMPOUNDS—Continued

Parameter ¹	EPA Method Number ^{2,3}			Other
	GC	GC/MS	HPLC	
49. 2,4-Dimethylphenol	604	625, 1625		
50. Dimethyl phthalate	606	625, 1625		
51. Di-n-butyl phthalate	606	625, 1625		
52. Di-n-octyl phthalate	606	625, 1625		
53. 2,4-Dinitrophenol	604	625, 1625		
54. 2,4-Dinitrotoluene	606	625, 1625		
55. 2,6-Dinitrotoluene	606	625, 1625		
56. Epichlorohydrin				Note 3, p. 130; Note 6, p. 5102
57. Ethylbenzene	602	624, 1624		
58. Fluoranthene	610	625, 1625	610	
59. Fluorene	610	625, 1625	610	
60. Hexachlorobenzene	612	625, 1625		
61. Hexachlorobutadiene	612	625, 1625		
62. Hexachlorocyclopentadiene	612	625, 1625		
63. Hexachloroethane	612	625, 1625		
64. Idenol(1,2,3-cd)pyrene	610	625, 1625	610	
65. Isophorone	606	625, 1625		
66. Methylene Chloride	601	624, 1624		Note 3, p. 130;
67. 2-Methyl-4,6-Dinitrophenol	604	625, 1625		
68. Naphthalene	610	625, 1625		
69. Nitrobenzene	606	625, 1625		
70. 2-Nitrophenol	604	625, 1625		
71. 4-Nitrophenol	604	625, 1625		
72. N-Nitrosodimethylamine	607	625, 1625		
73. N-Nitrosod-n-propylamine	607	625, 1625		
74. N-Nitrosodphenylamine	607	625, 1625		
75. 2,2-dicyclo(1-chloropropene)	611	625, 1625		
76. PCB-1016	606	625		Note 3, p. 43;
77. PCB-1221	606	625		Note 3, p. 43;
78. PCB-1232	606	625		Note 3, p. 43;
79. PCB-1242	606	625		Note 3, p. 43;
80. PCB-1248	606	625		Note 3, p. 43;
81. PCB-1254	606	625		Note 3, p. 43;
82. PCB-1260	606	625		Note 3, p. 43;
83. Pentachlorophenol	604	625, 1625		Note 3, p. 140;
84. Phenanthrene	610	625, 1625	610	
85. Phenol	604	625, 1625		
86. Pyrene	610	625, 1625	610	
87. 2,3,7,8-Tetrachlorodibenzo-p-dioxin		613		
88. 1,1,2,2-Tetrachloroethane	601	624, 1624		Note 3, p. 130;
89. Tetrachloroethene	601	624, 1624		Note 3, p. 130;
90. Toluene	602	624, 1624		
91. 1,2,4-Trichlorobenzene	612	625, 1625		Note 3, p. 130;
92. 1,1,1-Trichloroethane	601	624, 1624		
93. 1,1,2-Trichloroethane	601	624, 1624		Note 3, p. 130;
94. Trichloroethene	601	624, 1624		
95. Trichlorofluoromethane	601	624		
96. 2,4,6-Trichlorophenol	604	625, 1625		
97. Vinyl Chloride	601	624, 1624		

¹All parameters are expressed in micrograms per liter (µg/L).²The full text of Methods 601-613, 624, 625, 1624, and 1625 are given at Appendix A, "Test Procedures for Analysis of Organic Pollutants," of this Part 136. The standardized test procedure to be used to determine the method detection limit (MDL) for these test procedures is given at Appendix B, "Definition and Procedure for the Determination of the Method Detection Limit," of this Part 136.³Methods for Benzidine Chlorinated Organic Compounds, Pentachlorophenol and Pesticides in Water and Wastewater," U.S. Environmental Protection Agency, September, 1978. Method 624 may be extended to screen samples for Acroline and Acrylonitrile. However, when they are known to be present, the preferred method for these two compounds is Method 603 or Method 1624.⁴Method 625 may be extended to include benzidine, hexachlorocyclopentadiene, N-nitrosodimethylamine, and N-nitrosodphenylamine. However, when they are known to be present, Methods 605, 607, and 612 or Method 1625 are preferred methods for these compounds.⁵625, Screening only.⁶Selected Analytical Methods Approved and Cited by the United States Environmental Protection Agency, "Supplement to the Fifteenth Edition of Standard Methods for the Examination of Water and Wastewater (1981).⁷Each analyst must make an initial, one-time, demonstration of their ability to generate acceptable precision and accuracy with Methods 601-613, 624, 625, 1624, and 1625 (See Appendix A of this Part 136) in accordance with procedures each in section 8.2 of each of these Methods. Additionally each laboratory, on an on-going basis must spike and analyze 10% (5% for Methods 624 and 625 and 100% for methods 1624 and 1625) of all samples to monitor and evaluate laboratory data quality in accordance with sections 8.3 and 8.4 of these Methods. When the recovery of any parameter falls outside the warning limits, the analytical results for that parameter in the unspiked sample are suspect and cannot be reported to demonstrate regulatory compliance.

Note.—These warning limits are promulgated as an interim final action with a request for comments."

TABLE F4.—LIST OF APPROVED TEST PROCEDURES FOR PESTICIDES ¹

Parameter (µg/L)	Method	EPA ¹	Standard Methods 15th Ed	ASTM	Other
1 Aldrin	GC	608	508A	D3086	Note 3, p. 7, Note 4, p. 30.
	GC/MS	625			
2 Atrazine	GC				Note 3, p. 63, Note 6, p. S68.
3 Atrazine	TLC				Note 3, p. 94, Note 6, p. S16.
4 Atrazine	GC				Note 3, p. 63, Note 6, p. S68.
5 Atrazine	GC				Note 3, p. 63, Note 6, p. S68.
6 Azinphos methyl	GC				Note 3, p. 25, Note 6, p. S51.
7 Barben	TLC				Note 3, p. 104, Note 6, p. S64.
8 α-BHC	GC	608	508A	D3086	Note 3, p. 7.
	GC/MS	625			
9 β-BHC	GC	608		D3086	
	GC/MS	625			
10 δ-BHC	GC	608		D3086	

TABLE F4.—LIST OF APPROVED TEST PROCEDURES FOR PESTICIDES ¹—Continued

Parameter µg/L)	Method	EPA **	Standard Methods 15th Ed	ASTM	Other
11 γ-BHC (Lindane)	GC/MS	625			
12 Captan	GC	608	509A	D3086	Note 3, p. 7, Note 4, p. 30.
13 Carbaryl	GC/MS	625			
14 Carbophenothion	GC		509A		Note 3, p. 7
15 Chlordane	TLC				Note 3, p. 84, Note 6, p. S60.
16 Chlorpyrifos	GC				Note 4, p. 30, Note 6, p. S73.
17 2,4-D	GC	608	509A	D3086	Note 3, p. 7.
18 4,4'-DDD	GC/MS	625			
19 4,4'-DDE	TLC				Note 3, p. 104, Note 6, p. S64.
20 4,4'-DDT	GC		509B		Note 3, p. 115, Note 4, p. 35.
21 Demeton-O	GC	608	509A	D3086	Note 3, p. 7, Note 4, p. 30.
22 Demeton-S	GC/MS	625			
23 Diazinon	GC	608	509A	D3086	Note 3, p. 7, Note 4, p. 30.
24 Dicamba	GC/MS	625			
25 Dichlorfention	GC	608	509A	D3086	Note 3, p. 7, Note 4, p. 30.
26 Dichloran	GC	625			
27 Dicrofol	GC	608	509A	D3086	Note 3, p. 7, Note 4, p. 30.
28 Dieldrin	GC/MS	625			
29 Disulfoton	GC	608	509A	D3086	Note 3, p. 7, Note 4, p. 30.
30 Disulfoton	GC	625			
31 Diuron	GC/MS	608	509A	D3086	Note 3, p. 7, Note 4, p. 30.
32 Endosulfan I	GC	625			
33 Endosulfan II	GC/MS	625			
34 Endosulfan sulfate	GC	608	509A	D3086	Note 3, p. 7.
35 Endrin	GC/MS	625			
36 Endrin aldehyde	GC	608	509A	D3086	Note 3, p. 7, Note 4, p. 30.
37 Ethion	GC/MS	625			
38 Fenuron	GC	608	509A	D3086	Note 3, p. 7, Note 4, p. 30.
39 Fenuron-TCA	TLC				Note 4, p. 30, Note 6, p. S73.
40 Heptachlor	GC	608	509A	D3086	Note 3, p. 104, Note 6, p. S64.
41 Heptachlor epoxide	GC/MS	625			Note 3, p. 7, Note 4, p. 30.
42 Isodrin	GC	608	509A	D3086	Note 3, p. 7, Note 4, p. 30; Note 6, p. S73.
43 Linuron	GC/MS	625			
44 Malathion	GC	608	509A	D3086	Note 3, p. 7, Note 4, p. 30; Note 6, p. S73.
45 Methocarb	GC	608	509A	D3086	Note 3, p. 7, Note 4, p. 30.
46 Methoxychlor	GC	608	509A	D3086	Note 3, p. 7, Note 4, p. 30.
47 Methylcarbamate	GC	608	509A	D3086	Note 3, p. 7, Note 4, p. 30.
48 Mirex	GC	608	509A	D3086	Note 3, p. 7, Note 4, p. 30.
49 Monuron	TLC				Note 3, p. 104, Note 6, p. S64.
50 Monuron-TCA	TLC				Note 3, p. 104, Note 6, p. S64.
51 Neburon	TLC				Note 3, p. 104, Note 6, p. S64.
52 Parathion methyl	GC	608	509A	D3086	Note 3, p. 25, Note 4, p. 30.
53 Parathion ethyl	GC	608	509A	D3086	Note 3, p. 25.
54 PCNB	GC	608	509A	D3086	Note 3, p. 7.
55 Perthane	GC	608	509A	D3086	Note 3, p. 7.
56 Prometon	GC	608	509A	D3086	Note 3, p. 83, Note 6, p. S68.
57 Prometryn	GC	608	509A	D3086	Note 3, p. 83, Note 6, p. S68.
58 Propazine	GC	608	509A	D3086	Note 3, p. 83, Note 6, p. S68.
59 Propham	GC	608	509A	D3086	Note 3, p. 104, Note 6, p. S64.
60 Propoxur	TLC				Note 3, p. 94, Note 6, p. S60.
61 Sebumeton	TLC				Note 3, p. 83, Note 6, p. S68.
62 Scluron	TLC				Note 3, p. 104, Note 6, p. S64.
63 Simazine	GC	608	509A	D3086	Note 3, p. 83, Note 6, p. S68.
64 Strobane	GC	608	509A	D3086	Note 3, p. 7.
65 Sweep	GC	608	509A	D3086	Note 3, p. 7.
66 2,4,5-T	GC	608	509A	D3086	Note 3, p. 104, Note 6, p. S64.
67 2,4,5-TP (Silvex)	GC	608	509A	D3086	Note 3, p. 115, Note 4, p. 35.
68 Terbutylazine	GC	608	509A	D3086	Note 3, p. 83, Note 6, p. S68.
69 Toxaphene	GC	608	509A	D3086	Note 3, p. 7, Note 4, p. 30.
70 Trifluralin	GC/MS	625			Note 3, p. 7.

¹ Pesticides are listed in this table by common name for the convenience of the reader. A full-line version may be found in Table K, where entries are listed by chemical name.

* The full text of methods 60P and 61, 8-A-C can be found in Appendix A. The full text of methods 60P and 61, 8-A-C can be found in Appendix A.

² Methods for Benzidine Chlorinated Organic Compounds, Benzo(a)pyrene, and Benzo(a)anthracene in Water and Wastewater, U.S. Environmental Protection Agency, September, 1978. The

EPA publication includes thin layer chromatography (TLC) method for the analysis of organic substances in water. U.S. Environmental Protection Agency, Office of Water, Office of Research and Development, Report 823 (1972).

* The method may be extended to include a RHC & RHF exclusion (and sulfur and a sulfur element when they are known to exist. Method 608 is the preferred method.

* Selected Analytical Methods Approved and Cited by the United States Environmental Protection Agency, Supplement to the Fifteenth Edition of Standard Methods for the Examination of Water and Wastewater (1981).

¹ Each analyst must make an initial one-time demonstration of their ability to generate acceptable precision and accuracy with Methods 606 and 624 (See Appendix A of the Part 136) and

Method 508 or 5% of all samples analyzed with Method 525 to monitor and evaluate laboratory data quality in accordance with Sections 8.3 and 8.4 of these methods. When the recovery of

any parameter falls outside the warning limits, the analytical results for that parameter in the analyzed sample are suspended and not be reported to demonstrate regulatory compliance.

Note.—These warning limits are promulgated as an interim final action with a request for comments.

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TABLE F5.—LIST OF APPROVED RADIOLOGICAL TEST PROCEDURES

Parameter and units	Methods	EPA ¹	Reference (method No. or page)		
			Standard Methods 15th Ed.	ASTM	USGS ²
1. Alpha-Total, pCi per liter	Proportional or scintillation counter	900.0	703	D1943-66	pp. 75 and 78. ³
2. Alpha-Counting error, pCi per liter	Proportional or scintillation counter	Appendix B	703	D1943-66	p. 79.
3. Alpha-Counting error, pCi per liter	Proportional counter	900.0	703	D1890-66	pp. 75 and 78. ³
4. Beta-Counting error, pCi per liter	Proportional counter	Appendix B	703	D1890-66	p. 79.
5. (a) Radium-Total, pCi per liter	Proportional counter	903.0	705	D2480-70	
(b) ²²⁶ Ra, pCi per liter	Scintillation counter	903.1	706	D3454-79	p. 81.

¹ "Prescribed Procedures for Measurement of Radioactivity in Drinking Water," EPA-600/4-80-032 (1980 update), U.S. Environmental Protection Agency, August 1980.

² Fehman, M.J. and Brown, Eugene, "Selected Methods of the U.S. Geological Survey of Analysis of Wastewaters," U.S. Geological Survey, Open-File Report 76-177 (1976).

³ The method found on p. 75 measures only the dissolved portion while the method on p. 78 measures only the suspended portion. Therefore, the two results must be added to obtain the "total."

TABLE F6—REQUIRED CONTAINERS, PRESERVATION TECHNIQUES, AND HOLDING TIMES

Parameter No./name	Container ¹	Preservation ^{2,3}	Maximum holding time ⁴
Table IA—Bacterial Tests:			
1-4. Coliform, fecal and total	P, G	Cool, 4°C, 0.008% Na ₂ S ₂ O ₅ ⁵	6 hours
5. Fecal streptococci	P, G	do	Do.
Table IB—Inorganic Tests:			
1. Acidity	P, G	Cool, 4°C	14 days
2. Alkalinity	P, G	do	Do.
4. Ammonia	P, G	Cool, 4°C, H ₂ SO ₄ to pH < 2	28 days
9. Biochemical oxygen demand	P, G	Cool, 4°C	48 hours
11. Bromide	P, G	None required	28 days
14. Biochemical oxygen demand, carbonaceous	P, G	Cool, 4°C	48 hours
15. Chemical oxygen demand	P, G	Cool, 4°C, H ₂ SO ₄ to pH < 2	28 days
16. Chloride	P, G	None required	Do.
17. Chlorine, total residual	P, G	do	Analyze immediately
21. Color	P, G	Cool, 4°C	48 hours
23-24. Cyanide, total and amenable to chlorination	P, G	Cool, 4°C, NaOH to pH > 12, 0.6g ascorbic acid ⁶	14 days ⁶
25. Fluoride	P	None required	28 days
27. Hardness	P, G	HNO ₃ to pH < 2, H ₂ SO ₄ to pH < 2	6 months
28. Hydrogen ion (pH)	P, G	None required	Analyze immediately
31, 43. Kjeldahl and organic nitrogen	P, G	Cool, 4°C, H ₂ SO ₄ to pH < 2	28 days
Table IC—Organic Tests:			
18. Chromium VI	P, G	Cool, 4°C	24 hours
35. Mercury	P, G	HNO ₃ to pH < 2	28 days
3, 5-8, 10, 12, 13, 19, 20, 22, 26, 29, 30, 32-34, 36, 37, 45, 47, 51, 52, 58-60, 62, 63, 70-72, 74, 75. Metals, except chromium VI and mercury	P, G	do	6 months
38. Nitrate	P, G	Cool, 4°C	48 hours
39. Nitrate-nitrite	P, G	Cool, 4°C, H ₂ SO ₄ to pH < 2	28 days
40. Nitrite	P, G	Cool, 4°C	48 hours
41. Oil and grease	G	Cool, 4°C, H ₂ SO ₄ to pH < 2	28 days
42. Organic carbon	P, G	Cool, 4°C, HCl or H ₂ SO ₄ to pH < 2	Do.
44. Orthophosphate	P, G	Filter immediately, Cool, 4°C	48 hours
46. Oxygen, Dissolved Probe	G. Rinse and top	None required	Analyze immediately
47. Winkler	do	Fix on site and store in dark	8 hours
48. Phenols	G only	Cool, 4°C, H ₂ SO ₄ to pH < 2	28 days
49. Phosphorus (elemental)	G	Cool, 4°C	48 hours
50. Phosphorus, total	P, G	Cool, 4°C, H ₂ SO ₄ to pH < 2	28 days
53. Residue, total	P, G	Cool, 4°C	7 days
54. Residue, Filterable	P, G	do	48 hours
55. Residue, Nonfilterable (TSS)	P, G	do	7 days
56. Residue, Settleable	P, G	do	48 hours
57. Residue, volatile	P, G	do	7 days
61. Silica	P	do	28 days
64. Specific conductance	P, G	do	Do.
65. Sulfate	P, G	do	Do.
66. Sulfide	P, G	Cool, 4°C add zinc acetate plus sodium hydroxide to pH > 9	7 days
67. Sulfite	P, G	None required	Analyze immediately
68. Surfactants	P, G	Cool, 4°C	48 hours
69. Temperature	P, G	None required	Analyze
73. Turbidity	P, G	Cool, 4°C	48 hours
Table ID—Organic Tests:			
13, 18-20, 22, 24-28, 34-37, 39-43, 45-47, 58, 66, 68, 69, 92-95, 97. Purgeable hydrocarbons	G. Teflon-lined septum	Cool, 4°C, 0.008% Na ₂ S ₂ O ₅ ⁵	14 days
6, 57, 90. Purgeable aromatic hydrocarbons	do	Cool, 4°C, 0.008% Na ₂ S ₂ O ₅ ⁵ , HCl to pH 2 ⁷	Do.
3, 4. Acroten and acrylonitrile	do	Cool, 4°C, 0.008% Na ₂ S ₂ O ₅ ⁵ , Adjust pH to 4-5 ¹⁰	Do.
23, 30, 44, 49, 53, 67, 70, 71, 83, 85, 96. Phenols ¹¹	G. Teflon-lined cap	Cool, 4°C, 0.008% Na ₂ S ₂ O ₅ ⁵	7 days until extraction, 40 days after extraction
7, 38. Benzidines ¹²	do	do	7 days until extraction ¹³
14, 17, 48, 50-52. Phthalate esters ¹⁴	do	Cool, 4°C	7 days until extraction, 40 days after extraction
72-74. Nitroaromatics ¹⁵	do	Cool, 4°C, store in dark, 0.008% Na ₂ S ₂ O ₅ ⁵	Do.
76-82. PCBs ¹⁶ acrylonitrile	do	Cool, 4°C	Do.
54, 55, 65, 66. Nitroaromatics and isophorone ¹⁷	do	Cool, 4°C, 0.008% Na ₂ S ₂ O ₅ ⁵ store in dark	Do.
1, 2, 5, 8-12, 22, 33, 58, 59, 64, 68, 84, 86. Polynuclear aromatic hydrocarbons ¹⁸	do	do	Do.
15, 18, 21, 31, 75. Halocarbon ¹⁹	do	Cool, 4°C, 0.008% Na ₂ S ₂ O ₅ ⁵	Do.
29, 35-37, 60-63, 91. Chlorinated hydrocarbons ²⁰	do	Cool, 4°C	Do.
87. TCDD ²¹	do	Cool, 4°C, 0.008% Na ₂ S ₂ O ₅ ⁵	Do.
Table IE—Pesticides Tests:			
1-70. Pesticides ²²	do	Cool, 4°C, pH 5-9 ²³	Do.
Table IF—Retrological Tests:			
1-5. Alpha, beta and radium	P, G	HNO ₃ to pH < 2	6 months

¹ Polyethylene (Pl) or Glass (G)² Sample preservation should be performed immediately upon sample collection. For composite or sequential samples, each aliquot should be preserved at the time of collection. When use of an automated sampler makes it impossible to preserve each aliquot, each chemical sample must be preserved by immediately adding an equal volume of preservative and sample splitting is required.³ When any sample is to be shipped by common carrier or sent through the United States Mail, it must comply with the Department of Transportation Hazardous Materials Regulations (49 CFR Part 171). The person offering such material for transportation is responsible for meeting such requirements. For the preservation requirements of Table II, the Office of Hazardous Materials, Maritime Transportation Bureau, Department of Transportation has determined that the following materials are not hazardous: Hydrochloric acid (HCl) in water solutions at concentrations of 0.04% by weight or less (pH about 1.2); acetic acid in water solutions at concentrations of 0.15% by weight or less (pH about 1.62) or greater; Sulfuric acid (H₂SO₄) in water solutions at concentrations of 0.01% by weight or less (pH about 1.7) or greater; and Sodium hydroxide (NaOH) in water solutions at concentrations of 0.10% by weight or less (pH about 12.3) or less.⁴ Samples should be analyzed as soon as possible after collection. The time between collection and analysis should be held below 24 hours. Samples may be held for longer periods only if the permittee or monitoring laboratory has data on file to show that the stability of the analytes under study are stable for the longer time, and has received a variance from the Department of Commerce or under a 10-day permit. Some samples may be held for up to 60 days for the purpose of the permit given in the table. A permittee or monitoring laboratory is obligated to hold the sample for a shorter period if evidence exists to show that this is necessary to maintain sample stability. See 49 CFR for details.⁵ Should only be used in the presence of residual chlorine.⁶ Maximum holding time is 24 hours when sulfide is present. Addition of samples may be made with lead acetate to remove sulfide. Adjustments in order to determine if sulfide is present if sulfide is present it can be removed by the addition of lead acetate to a negative spot test. (pH 12). The sample is filtered and then NaOH is added to pH 12.⁷ Samples should be filtered immediately on site before adding preservative to avoid loss of volatile organics.⁸ Surface A appears in samples to be analyzed by 49 CFR 171.15, 171.16, 171.17, 171.18, 171.19, 171.20, 171.21, 171.22, 171.23, 171.24, 171.25, 171.26, 171.27, 171.28, 171.29, 171.30, 171.31, 171.32, 171.33, 171.34, 171.35, 171.36, 171.37, 171.38, 171.39, 171.40, 171.41, 171.42, 171.43, 171.44, 171.45, 171.46, 171.47, 171.48, 171.49, 171.50, 171.51, 171.52, 171.53, 171.54, 171.55, 171.56, 171.57, 171.58, 171.59, 171.60, 171.61, 171.62, 171.63, 171.64, 171.65, 171.66, 171.67, 171.68, 171.69, 171.70, 171.71, 171.72, 171.73, 171.74, 171.75, 171.76, 171.77, 171.78, 171.79, 171.80, 171.81, 171.82, 171.83, 171.84, 171.85, 171.86, 171.87, 171.88, 171.89, 171.90, 171.91, 171.92, 171.93, 171.94, 171.95, 171.96, 171.97, 171.98, 171.99, 171.100.⁹ Samples requiring pH adjustment must be analyzed at the same time as the sample.¹⁰ The pH adjustment is not required if an acid will not be used and the sample for a sample requiring no pH adjustment must be analyzed within 3 days of sampling.¹¹ When the extractable analytes of concern fall within a sample, the maximum holding time for the sample should be observed for optimum safeguard of sample integrity. When the analytes of concern fall within two or more materials, the maximum holding time should be observed for the longest holding time. Exceptions to this rule: storing in the dark and adjusting the pH to 5-9. Samples preserved in this manner may be held for up to 60 days after collection. For the analysis of alpha, beta and radium, the maximum holding time is 6 months.¹² If 2,4-diaminodiphenylamine is only to be present, adjust the pH of the sample to 4-5. For the analysis of benzidine, adjust the pH to 12.¹³ If 2,4-diaminodiphenylamine is only to be present, adjust the pH of the sample to 4-5. For the analysis of benzidine, adjust the pH to 12.¹⁴ For the analysis of alpha, beta and radium, adjust the pH of the sample to 4-5. For the analysis of benzidine, adjust the pH to 12.¹⁵ The pH adjustment may be performed upon receipt at the laboratory and may be performed within 24 hours of collection. For the analysis of alpha, beta and radium, the maximum holding time is 6 months.Na₂S₂O₅

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